Title: Oxidative Coupling of Methane
Using Inorganic Membrane Reactors

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OBJECTIVE

The objective of this research is to study the oxidative coupling of methane in catalytic inorganic membrane reactors. A specific target is to achieve conversion of methane to C_2 hydrocarbons at very high selectivity and higher yields than in conventional non-porous, co-feed, fixed bed reactors by controlling the oxygen supply through the membrane.

A membrane reactor has the advantage of precisely controlling the rate of delivery of oxygen to the catalyst. This facility permits balancing the rate of oxidation and reduction of the catalyst. In addition, membrane reactors minimize the concentration of gas phase oxygen thus reducing non selective gas phase reactions, which are believed to be a main route for the formation of CO_x products. Such gas phase reactions are a cause of decreased selectivity in the oxidative coupling of methane in conventional flow reactors. Membrane reactors could also produce higher product yields by providing better distribution of the reactant gases over the catalyst than the conventional plug flow reactors.

Membrane reactor technology also offers the potential for modifying the membranes both to improve catalytic properties as well as to regulate the rate of the permeation/diffusion of reactants through the membrane to minimize by-product generation. Other benefits also exist with membrane reactors, such as the mitigation of thermal hot-spots for highly exothermic reactions such as the oxidative coupling of methane. The application of catalytically active inorganic membranes has potential for drastically increasing the yield of reactions which are currently limited by either thermodynamic equilibria, product inhibition, or kinetic selectivity.

APPROACH

In order to achieve the objective of obtaining higher C_2 selectivities and C_2 yields in the oxidative coupling of methane, the approach followed in this work was to use membrane reactor configurations that enable control of the supply of oxygen to the methane coupling reaction. Three reactor configurations were proposed to be studied. The first configuration was a packed bed reactor where the tube containing the catalyst bed was a porous membrane. The main function of the membrane in this configuration was to allow metering of the supply of oxygen. The second type of reactor was a dense membrane reactor. The dense membrane would be a material that was impervious to gases other than oxygen and thus would allow only oxygen to permeate across the membrane. The third configuration of the membrane reactor had the catalyst deposited inside the membrane pores. In all these membrane reactors, we set out to determine whether the methane conversion and hydrocarbon selectivity of the coupling reaction could be regulated by controlling the rate of oxygen transfer to the catalyst site.

Executive Summary

Oxidative coupling of methane (OCM) - direct conversion of methane to C_2 hydrocarbon in the presence of oxygen - is of great practice importance and is regarded as the most promising route to the utilization of our abundant natural gas resources. Although extensive R & D efforts have been made worldwide in this area, OCM is still not an economically and technologically feasible process due to the relatively low C_2 yield. It is generally recognized that C_2 yield of 35% or higher would be needed for the process to be economically viable. The application of membrane reactors has great potential to increase the desired product yield of reactions, which are limited by thermodynamic equilibrium, product inhibition, or kinetic selectivity due to undesired parallel and/or series reactions. In the present research program, oxidative coupling of methane was studied by using catalytic inorganic membrane reactors to achieve higher selectivity and yield towards C_2 hydrocarbons. The use of membrane reactor configurations enabled the control of the oxygen supply through the membrane and thus suppresses the further oxidation of the C_2 hydrocarbons. Thus, the membrane reactor offered the potential for higher C_2 selectivity than the conventional co-feed reactor.

Significant achievements have been made in all aspects of the project such as material synthesis, membrane preparation and modification, module design, as well as theoretical modeling. Both porous and dense ceramic membrane reactors were developed and experiments were conducted under different reactor configurations, operating conditions, and catalysts.

Methane oxidative coupling catalysts, different perovskites, and other oxygen conducting materials were synthesized by co-precipitation, sol-gel, and cavitation methods and characterized by XRD, SEM, EDX, DSC, as well as by permeation measurements. In addition to materials research, various membrane synthesis techniques, such as pore filling of porous membranes, stabilization of gamma alumina membranes, and preparation and modification of dense oxygen conducting membranes, were investigated.

A membrane reactor with thermally treated porous Vycor glass membrane tube was fabricated for the OCM study. The membrane had sufficient resistance to permeate gas flow and, therefore, provided a uniform supply of oxygen to the reaction side of the membrane reactor, which allowed the oxygen flow rate to be regulated by adjusting the pressure on the oxygen-feed side. Experimental results showed that under equivalent conditions, C_2 selectivities were 10% higher in the membrane reactor as compared to the conventional co-feed non-porous reactor in the temperature range 650°C to 850°C. Studies involving variation of methane to oxygen ratios showed that both the methane conversions and C_2 selectivities were highest at a methane to oxygen ratio of 2.0. Experiments run at conditions where the oxygen conversion was less than 100% resulted in lowered C_2 selectivity and higher methane conversions because of oxygen availability. Experiments involving metering of methane flow from the high-pressure shell side into a mixture of oxygen and helium on the catalyst packed tube side showed that improved hydrocarbon selectivity has overshadowed by a lowered methane conversion. These results indicate that metering the oxygen flow through porous membrane reactors is beneficial to the methane coupling reaction when most of the oxygen supplied to the catalyst bed is used up before exiting the reactor.

Oxygen-conducting dense membranes have the unique property of allowing selective permeation of oxygen, and a cheap oxygen source such as air can be used as the oxidant for OCM, while eliminating the contamination of the product by nitrogen. Two types of dense membrane reactors were used in the OCM studies. The first one was prepared using a non-perovskite material, $SrFeCo_{0.5}O_{3-\delta}$, which was a total oxidation catalyst. The oxygen flux was about 0.04 cc(STP)/min cm^2 at 950°C under non-reaction conditions. The oxygen flux increased with an increase in either the helium sweep flow rate, the air flowrate in the shell side, or temperature. When reactions took place in the membrane tube, the oxygen flux was found to be about four times higher than that observed under non-reaction conditions. In order to reduce the total oxidation of hydrocarbons catalyzed by the dense membrane material, a perovskite oxide material ($BaCe_{0.6}Sm_{0.4}O_3$) was coated on the inner wall of the dense membrane tube. La/MgO catalyst, which was prepared by a precipitation method, was packed inside the dense

membrane tube. Methane mixed with helium flowed in the tube side, while air was fed to the shell side. The oxygen flux values under non-reaction condition were only about 30% of those obtained with an uncoated dense membrane tube. Compared to the co-feed reactor configuration (i.e. co-feeding oxygen and methane to the tube side of the same membrane reactor setup) at the same methane conversion level, the membrane reactor gave higher C_2 selectivity in the low methane conversion region.

The second dense membrane material prepared was a perovskite material, $BaCe_{0.8}Gd_{0.2}O_3$, which was synthesized by the ethylene glycol method. Dense membrane tubes were fabricated using a plastic extrusion technique. OCM experimental results in the absence of additional catalyst showed that this material has fairly good catalytic activity. The oxygen permeance of the dense membrane tube was measured as a function of temperature and oxygen partial pressure on the feed side. In the temperature range of 688°C to 955°C, the dependence of oxygen flux on the temperature obeyed the Arrhenius law. The oxygen flux increased proportionally with the natural logarithm of the oxygen partial pressure in the feed side. Yields of the C_2 hydrocarbons up to 16% were achieved in the $BaCe_{0.8}Gd_{0.2}O_3$ dense membrane reactor.

A porous gamma alumina membrane reactor was employed to study the OCM with Mn-W-Na/SiO₂ catalyst packed inside the membrane tube. The gamma-alumina membrane tube was thermally stabilized by treating the membrane tube with La(NO₃)₃ aqueous solution and calcining at 900°C. C_2 yields up to 27.5% were achieved, which is the highest C_2 yield reported in literature for methane coupling with membrane reactors. Although the membrane reactor showed lower methane conversion than the co-feed fixed bed reactor at the same reaction conditions, it gave higher C_2 selectivity and C_2 yield at similar methane conversions.

A radial-flow membrane reactor was developed to study the effect of pore size (or flow regime) on the OCM performance. Sm₂O₃ catalyst was deposited in an asymmetric porous gamma-alumina membrane with pore diameters of 2.0 μm (50% Knudsen transport), 0.05 μm, and 0.02 μm (100% Knudsen transport). Depositing the catalyst in the relatively thin fine membrane layer also served to reduce contact of the desired C_2

products with oxygenated surfaces as they left the reaction zone. It was found that the smallest pore size were best for both conversion and selectivity, confirming the benefits of Knudsen contact regime. The yield was higher than that observed in the comparable packed-bed reactors with the same catalyst, which suggested that keeping the contact time short in the radial-flow catalytic membrane reactor was beneficial for OCM reactions.

A mathematical model was developed for the simulation of distributed feed reactors with six types of feed policies. All of the six types of cross-flow reactors were analyzed for general series-parallel reaction systems and their optimal feed distributions were determined by maximizing the desired product yield at the outlet of the reactor. Parameter studies identified regions in parameter space where the membrane reactors could outperform the non-porous co-feed reactors. Modeling studies on parametric evaluation for oxidative coupling of methane indicated that the membrane reactors perform better than the conventional non-porous packed bed reactors at sufficiently large residence times. Optimum concentration profiles for metered oxygen distribution were obtained for staged reactant feed streams.

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Chapter 1. Introduction

Conversion of methane, which is the main constituent of abundantly available natural gas, into valuable products has become an increasingly attractive proposition in recent years with rapid advancements in natural gas technology. World proven reserves of natural gas are over 100 trillion cubic meters [1, 2]. In BTU equivalents, the known reserves of natural gas are nearly equal to the reserves of crude oil [3] and could last about 75 years at the present consumption rate. However, the majority of these reserves is in remote locations where it cannot be used directly. Due to its low energy content per unit volume, it is uneconomic to transport natural gas from the wellheads to the consumers unless chemically converted to liquid products to facilitate the transportation and enhance the value of energy content per unit volume. As a result, only about 7% of the world production of methane is used in the chemical industries [4] and the remainder is burned as fuel for heating and power generation. Methane flaring or emission causes not only a wastage of valuable energy but also global warming due to the release of very large quantities of CO_2 in the atmosphere. The direct conversion of methane to more useful chemicals and fuels has been recognized as one of the most technologically important and challenging problems facing industrialized nations in the latter part of the twentieth century.

Methane can be converted into the following easily transportable products: 1. methanol (as fuel or feed stock for petroleum and petrochemicals); 2. liquid hydrocarbon fuels (gasoline, diesel, kerosene, etc.); 3. ethylene and other lower olefins, which can be used as feed stock for petrochemicals and /or petroleum products; and 4. syn-gas (a mixture of CO and H_2), which is a versatile feed stock for methanol and ammonia synthesis and Fischer-Tropsch synthesis products like liquid hydrocarbons, oxygenates, etc. So far none of the direct methane conversion routes have been commercialized except syn-gas production.

1.1 Literature Review

1.1.1 Historical Preview

The systematic study of the direct conversion of methane to obtain more valuable products started at the beginning of this century and considerable research was carried out in the 1920s and 1930s [5]. Direct methane conversion may be grouped into two categories: thermal and catalytic conversion. The thermal cracking reactions are endothermic and temperature has to be above 1000°C and reaction time must be very short to avoid carbon formation. These conditions and the large quantities of energy required make this process costly. Thermal conversion of methane by oxygen can lead to methanol, formaldehyde and C₂+ hydrocarbons, but selectivities to these products are quite low due to deep oxidation reactions. Catalytic pyrolysis of methane on solid catalyst is not a practical approach because of the high temperature required and the problem of carbon formation on the catalyst. The direct conversion of methane/oxygen mixture to methanol and formaldehyde has also received significant attention. These reactions are often called partial oxidation of methane since the methanol and formaldehyde synthesis requires the formation of carbon-oxygen bond. There has also been interest in the conversion of methane by using non-oxygen reagents such as poly-oxometalates [6], nitrous oxide (N₂O) [7, 8, 9], halogens [10, 11], sulfur or ammonia [12], and other hydrocarbons such as acetylene [13]. However, none of them has yet been shown to be effective and economical. The electrochemical conversion of methane to higher hydrocarbons is another possible route for the utilization of natural gas. Nonetheless, the conversion of methane using oxygen as the oxidant to higher hydrocarbons through heterogeneous catalysis has proved more successful than the other routes, and consequently has been intensively studied. Oxidative coupling of methane (OCM) is one of the more recent and potentially attractive processes that provides much promise for the utilization of methane feedstocks found abundantly in nature.

1.1.2 Catalytic Methane Coupling

The preferred route for methane conversion is by heterogeneous catalysis. It is possible to react methane in the gas phase by thermal means; however, the process is energy-intensive, as it requires temperatures of over $1,000^{\circ}\text{C}$, and is highly non-selective. The great majority of catalysts for methane coupling become active only at temperatures above 700°C .

The OCM process involves the metal-oxide catalyzed reaction of methane in the presence of oxygen to form C_2 hydrocarbons (C_2H_4 and C_2H_6), along with the oxygenated products CO , CO_2 and H_2O . Increasing methane conversion however, is accompanied by lowered C_2 selectivity and the resulting decrease in C_2 yield is characteristic of such reactions where the intermediate products (C_2H_4 , C_2H_6) are more reactive than the reactants (CH_4). The term oxidative coupling arises from the use of oxygen as a co-reactant in this process. The oxygen consumes some hydrogen to form water, following C-H bond fission of the methane on the catalyst. Unfortunately, the current generation of catalysts require temperatures in excess of 750°C before their activity is sufficiently high enough to give commercially acceptable levels of conversion. At these temperatures, the complete oxidation of CH_4 , and even more readily of the C_2 -hydrocarbon products to CO_2 , is difficult to avoid. Methane coupling has, therefore, been limited up to now to low conversions, in order to achieve reasonable selectivity.

Since the reaction mechanism requires the presence of oxygen, unavoidable side products such as CO and CO_2 that are formed, both adversely affect the economics of the process through lowered selectivity, and also present a waste disposal problem. In the last decade, oxidative coupling of methane to C_2 hydrocarbons has attracted tremendous enthusiasm around the world. This period saw an exponentially increasing interest in the OCM technology as evidenced by the reported work in the literature [1-30]. An excellent

review on the evolution and current state of research in the OCM technology is given by Amenomiya *et al.* [14]. Extensive R & D efforts in this area have been made and significant success has been achieved [31, 32, 3, 33, 34, 35]. According to previous reactor designs, the OCM reactions can be carried out in two operational modes: cyclic feed and co-feed operation, and most of the OCM experiments were focused on the co-feed mode. Since the publication of the first systematic screening of metal oxides for OCM by Keller and Bhasin [36], the number of papers dealing with this subject has dramatically increased [5, 12, 14, 31, 32, 37, 38, 39, 40, 41].

1.1.3 Challenges for Commercialization

The challenges that limit the commercialization of OCM process are: (1) high temperature (750~800°C) to achieve high C₂ yield; (2) removal of the heat generated by the highly exothermic reactions to control the hot-spot temperature, which may limit the highest oxygen inlet concentration and decrease the selectivity; (3) limitation on methane conversion (<40%) and C₂ yield (<25%) imposed by the explosion limit of oxygen concentration in the feed; (4) low concentration of ethylene in the product (<7~8%) making the product separation by conventional cryogenic processes uneconomical; (5) low selectivity at high conversion making simultaneously achieving good selectivity and conversion extremely difficult; and (6) short life time for catalysts containing volatile promoters.

Engineering and economic performance of OCM depends critically on the conversion and selectivity, as well as the price of natural gas relative to that of crude oil. It was estimated that single-pass conversions of 35~37% and selectivities of 85~88% (equivalent to 30+% C₂ yield) are required to achieve commercial feasibility [42, 43]. High C₂ yields can be achieved by increasing methane conversion, C₂ selectivity, or both. Unfortunately, as discussed earlier higher selectivity is usually obtained at lower conversion. Many researchers believe that C₂ selectivity is the more important factor in practical applications of OCM because unreacted methane can always be separated and

recycled. High C_2 yields may be achieved by the design and development of better catalysts, product removal, CH_4 recycle, and new reactor designs such as distributed feed of oxygen and the use of membrane reactors.

While a strong interest in catalyst investigation and mechanistic study are the focus of research at one end of the spectrum [1- 43], the overall process yield of the valuable C_2 hydrocarbons is the driving force for a lot of the process research and innovative reactor designs [44-51]. Section 1.1.5 details some of the literature studies on methane coupling catalysts and Section 1.1.6 discusses some developments on catalysts used for methane coupling research while Section 1.1.7 deals with novel reactor design approaches for development of OCM technology.

1.1.4 Mechanism of Methane Coupling

Thorough reviews of the methane dimerization (OCM) system have appeared recently [14, 39, 52]. High temperature reactions occurring during methane coupling consist of a complex set of reactions, both gas phase homogeneous reactions as well as catalyzed heterogeneous reactions, involving the presence of methyl radicals [53-56]. A wide variety of catalysts has been studied, however there is general agreement as to the main features of the process.

Methane is activated by adsorption onto the catalyst surface at an active site (e.g. $[Li^+O^-]$), followed by C-H bond fission and desorption into the gas phase of methyl radicals. These may then combine to form C_2H_6 in the gas phase or on the surface. Early work was directed towards study of surface reactions [36, 57]). More recently Mackie [58] has reviewed the literature results on gas-phase reactions and concluded that a significant fraction of the total reaction takes place in the gas phase, especially at higher temperatures ($> 850^\circ C$).

The non-selective CO_x products can arise from surface reactions of methyl radicals with oxygen or by secondary gas phase oxidation of the C_2 species. It is likely that CO/CO_2 is a direct product of CH_4 partial oxidation as well as a product of C_2 oxidation. Mackie [58] has concluded that at temperatures above 740°C , between 30% and 80% of the CO_x is attributed to gas phase oxidation of C_2 molecules, while at temperatures below 700°C there is surface promoted reaction between CH_4 and O_2 forming CO_2 .

Various mechanisms of methyl radical activation have been proposed [19, 20, 22, 30], based on the different kinds of oxygen species that could be formed during the high temperature OCM reactions: the lattice oxygen O^{2-} , the dioxygen anion radical (O_2^-), the peroxide ion (O_2^{2-}), and atomic oxygen (O^-). The review by Voskrsenskaya *et al* [22] summarizes the different views on the roles of these oxygen species in the overall reaction mechanism of methane coupling. Structural defects on the oxide [22], gas phase oxygen partial pressure [23], the influence of deep oxidation products CO/CO_2 [18], etc., are all believed to be responsible for the oxidant activation for methane coupling.

1.1.5 Review of OCM Catalysts

Most of the effort devoted in OCM studies so far has been the determination of catalytic performance of catalyst and characterization, reaction mechanism and catalyst screening. Catalysts which are both active and selective for OCM may be described as strongly basic metal oxides. By now the periodic table has been visited extensively in catalyst screening studies. By their locations in the periodic table, catalysts for methane coupling can be divided into three major groups [14].

(1) Alkali and alkaline earth metal compounds. Li/MgO is the most frequently used catalyst in this group. For Na/MgO , a 22.4% C_2 yield has been reported [59, 60].

The combination of Li and lanthanide promoters for MgO gives C₂ selectivity of 98.4% at conversion of 25% [61].

(2) The compounds of lanthanide and actinide metals. Sm₂O₃ is the most effective of the lanthanide oxides due to its basicity. Promotion by lithium salts, especially LiCl, further enhances the utility of the catalyst at low pressures. The promoted lanthanide oxides seem to be the most promising catalysts because of their high stability as well as high selectivity and activity. A Perovskite-type oxide SrCe_{0.9}Yb_{0.1}O₃ was reported to give 31.6% C₂ yield with C₂ selectivity of 60.1% [62], although this performance could not be confirmed in our laboratory.

(3) Compounds of transition metals and those of post-transition metals. The transition metal oxides (except manganese oxide) are normally effective as catalysts for non-selective oxidation. However, when supported, promoted (e.g. LiCl/TiO₂), or present as composite materials, significant activity for OCM has been achieved. Promotion of MnO_x with NaCl [63] or LiCl [64] gave C₂ selectivity up to 65.2% at 1023K and for O₂/CH₄ ratio close to 0.5. MnO/NaCl/TiO₂ gave 26.4% C₂ yield at 750°C and CH₄/O₂=2.75 [65]. Molten salts are formed under OCM conditions using MnSO₄/Na₂SO₄ and 57% selectivity was obtained at 24.5% conversion and 1179 K [66]. On Li₂SO₄-Mn_xO_y/TiO₂ catalyst, a yield of 35.5% with selectivity of 75.8% was reported [67]. Using diatomite as the support, the same catalyst gave 38.9% C₂ yield and 92.3% C₂ selectivity [64]. For Fe₂O₃ or Co₂O₃ alone, no coupling activity was observed. Significant C₂ yield was observed when Co₂O₃ was promoted with LiCl, but when Fe₂O₃ was promoted by alkali metal nitrates, the selectivity was very low. Silver catalysts (Ag, Ag₂O, or supported Ag) are ineffective for methane coupling. Lead oxide supported on alumina has been used extensively and its activity varies with methane and oxygen pressures, temperature, and the presence of additives. Bismuth-containing oxides are also promising OCM catalysts [68].

1.1.6 Catalyst Design

The most important parameters affecting the oxidative coupling of methane include the temperature, the pressure, the CH_4/O_2 ratio and the residence time. Catalyst activity always increases with temperature and C_2 selectivity generally increases with temperature from 600–800°C. This is due to the fact that the activation energy of C_2 formation is much higher than that of CO_x formation. At higher temperature, the selectivity behavior is more ambiguous since the contribution of gas phase reactions to the overall reaction becomes greater. An increase in total pressure increases the methane conversion rate, but usually decreases the selectivity. The temperature range in which the gas phase reactions become predominant shifts to lower temperatures at elevated pressures. Thus the use of a large fraction of inert gas as diluent generally leads to higher selectivity [69]. A higher CH_4/O_2 ratio increases the C_2 selectivity but naturally decreases the percent conversion. An increase in residence time increases the conversion, but the selectivity decreases because the C_2 formed is much more reactive than methane.

Although the chemistry of the methane dimerization (OCM) process is very complex, and dependent upon specific process conditions and choice of catalyst, the above observations form a basis for the discussion of processing technologies for enhanced conversion and selectivity in this system. It is clear that gas phase reactions are dominant for oxidative coupling at high temperatures. In particular, a large amount of non-selective product CO_x is formed in the gas phase. Unfortunately, the most convenient way to increase CH_4 conversion is to increase temperature. Decreasing the CH_4/O_2 ratio in the gas feed also increases conversion, but at the expense of selectivity.

The above reasoning has led many researchers to attempt to develop catalysts that will be active for methane coupling at relatively low temperatures, so that gas phase reactions will be eliminated. In addition, if the amount of oxygen in the bulk gas can be reduced, there will be a decrease in the concentration of adsorbed molecular oxygen (M-

O-O-), which several workers have suggested may be responsible for CO₂ production [39].

A recent study is that of Pereira *et al.* [55], who obtained 10% CH₄ conversion at near 100% selectivity to higher hydrocarbons, over a calcium /nickel/ potassium oxide catalyst at temperatures close to 600°C. Although the overall yield per pass was quite small (~10%), no previous work had approached conversion this high at comparable selectivities. The elimination of CO₂ scrubbing from the treatment of the recycle CH₄ gas makes this approach attractive from the standpoint of process design and economics.

The results of Pereira *et al.*, [55] present some interesting points. First, the conversion per pass remains low. At higher temperatures than 600°C, conversion could be increased but selectivity was lost. This suggests that surface reactions to CO_x rapidly become important as temperature increases, even with low amounts of fed O₂. Second, the nature of the surface sites appears critical, as steam was essential in the reactor feed to obtain any CH₄ conversion, implying that the surface was modified by hydroxyl species. Third, the ratio of olefins to paraffins was quite low, consistent with the discussion above. The low oxygen partial pressure would not favor oxidation of ethane to ethylene.

Catalytic performance is dependent on reaction conditions, catalyst composition, and preparation parameters such as precursors and the calcination temperature and atmosphere. This makes the catalyst evaluation and activity comparison more difficult. In addition, it is very difficult, if not impossible, for most of the surface characterization techniques (ESCA, TEM, SEM, etc.) to perform at the high OCM temperature conditions. Therefore, there is no direct relationship between the characterized surface properties and the activity/selectivity in OCM that has been observed. To make things even more complicated, the gas-phase homogeneous reactions can play a significant role in OCM and their extent relative to surface reactions depends on the temperature, total and partial pressures of reactants, residence time, and the free volume of reactor, etc. There is no

simple mechanism to describe this homogeneous-heterogeneous reaction system. Due to the high conversion of oxygen and the interaction between homogeneous and heterogeneous reactions, it is usually difficult to obtain kinetic equations experimentally for OCM. As a result, the catalyst design/development has been done mostly by manipulating catalyst composition like promoters and its concentration and preparation parameters.

It may be concluded that even after a great deal of catalyst development, it is still not possible to achieve high conversion and selectivity simultaneously in co-fed conventional reactor systems. At high temperatures, oxygen in the gas phase leads to non-selective products, while at low temperatures the solid surface reaction picture appears to be rather complex and has so far restricted results to low conversions. For these reasons, it is attractive to consider alternative reactor configurations, such as membrane reactors, which can separate hydrocarbon and oxygen bulk gas streams.

1.1.7 Reactor Design, Distributed Feed of Oxygen and the Use of Membrane Reactors

One of the key challenges for the industrial application of OCM is the heat management and temperature control. It was shown by runaway analysis that the required tube diameter in a fixed-bed tubular reactor is too small to be practical [47]. Proposed methods to cope with the heat removal problem include the use of single- or multi-stage fluidized-bed reactors [70] and reactors in series with inter-stage cooling.

Heterogeneous reactions in OCM become more important at higher temperature. So, the free volume and surface to volume ratio in the catalyst bed is a very important factor for reactor design, and it will ultimately affect the obtained C_2 yield. The blank tests without catalyst showing little or negligible amount of product are somewhat misleading. The reaction in an empty reactor is limited by the poor production of methyl radicals. Once the formation of CH_3 is initiated, the gas phase reactions proceed extensively. Thus, measures should be taken for rapid removal of products from the

reaction zone to minimize the post-catalytic deep oxidation of C_2 hydrocarbons. The effect of volume-to-surface ratio was demonstrated by Chou and Albright [71]. They observed that upon packing a tubular bed with Pyrex beads the conversion of methane at 540°C decreased from 85% to 0.2% at the same residence time (Same inlet flow or same residence time).

As indicated by the OCM kinetics (Section 1.3), the reaction order in O_2 for methane coupling is lower than that for the total methane oxidation reaction. So, lower oxygen partial pressure will result in higher C_2 selectivity, which could be realized by introducing oxygen at injection ports along the reactor length or using a membrane reactor with its wall as a oxygen distributor. Most of the modeling studies [48, 72, 73, 74, 75, 76] show that distributed feed of oxygen results in an increase in C_2 selectivity and yield.

A small number of studies have attempted to regulate the supply of oxygen to the active catalytic sites using membranes. A membrane that is semi-permeable to oxygen can be formed by a thin, dense film of an anionic conductor such as stabilized zirconia. Of particular interest is the study of Stoukides and Vayenas [77], who looked at electrochemical pumping of oxygen through a silver coated zirconia cell for the partial oxidation of ethylene. This cell required an external voltage to be applied to pump O^{2-} to the catalyst. Dramatic increases were observed in both reaction rate and selectivity to ethylene oxide. These increases were attributed to changes in the properties of the catalyst when oxygen pumping took place. It appeared that a surface layer of silver oxide was formed that had high activity for the epoxidation reaction. This result suggests some interesting possibilities for the modification of methane dimerization catalysts.

The first experimental study showing the beneficial effect of distributed oxygen feed on methane conversion and C_2 selectivity was done by Choudhary *et al* [49] in four tubular reactors connected in series with La/MgO as the catalyst. For a fixed overall ratio

of methane to oxygen, the C_2 yield increased as the number of oxygen feed points increased. Smith *et al.* [78] found that introducing additional oxygen at the midpoint of a Li/Pb/Ca catalyst fixed-bed reactor increased C_2 space time yield more than CO_x space time yield. They also introduced 50 ml/min of He/O (93:7) to the mid point of a La_2O_3 /PbO/CaO catalyst bed receiving 50 ml/min He/ CH_4 /O (80:13:7) at 700°C and observed a 64% increase in C_2 selectivity over a run with no auxiliary gas. They attributed this improvement in C_2 selectivity to the increase of methyl radical generation on the O_2 replenished catalyst surface. Similar results were obtained by Santos *et al.* [79] who found that with an appropriate choice of reaction conditions the yields obtained with the distributed feed reactor were found to be higher than those with a single feed reactor. A three-stage reactor packed with Li/MgO catalyst was used by Matsura *et al.* [80] to improve yield and 49% methane conversion and 60% C_2 hydrocarbon yield were obtained. The methane flow rate was 30ml/min and 8:1 mixtures of He and O_2 at 70, 56, and 45 ml/min were introduced to the first, second, and third stage, respectively. Mleczko *et al.* [76, 81]) studied both fixed and fluidized-bed reactors operated in two different modes: co-feed of CH_4 and O_2 and distributed feed of O_2 with three catalysts: PbO/ α - Al_2O_3 , NaOH/CaO, and La_2O_3 /CaO. The distributed feed resulted in a marked increase of selectivity and yield. The experimental studies on a fluidized bed reactor by Do *et al.* [82] showed that for the same total input of oxygen, the performance of a single stage and a two-stage fluidized-bed reactor with inter-stage addition of oxygen were the same for different catalysts over a wide range of reaction conditions. Campbell and Ekstrom [83] carried out methane coupling in five tubular reactors connected in series and they did not believe that distributed oxygen feed could significantly improve the C_{2+} yield.

1.1.7.1 Dense Membrane Reactors for OCM

Since 1989 Fujimoto and his co-workers have reported studies on methane oxidative coupling using dense membrane reactors ([84, 85]. Although most of the C_2

selectivity data they reported are very high ($> 90\%$), the methane conversions were too low (about 0.5%) to be industrially feasible.

Using a proton-hole mixed conductor ($\text{Sr}_{0.95}\text{Yb}_{0.05}\text{CeO}_{3-\delta}$) as a membrane reactor, Iwahara and his co-workers [86, 87] and Chiang *et al.* [88, 89] carried out methane coupling reactions. The formation of C_2 hydrocarbon was enhanced by the permeation of hydrogen and the removal of hydrogen by reacting with oxygen in the side opposite to the methane-feeding side of the membrane. Although there were no carbon oxides formed, the conversion was less than 1% due to the equilibrium limitation and low activity of the catalyst they used.

Anshits *et al* [90, 91]) investigated the methane coupling reaction through a silver membrane reactor. At methane conversions of 0.03 and 3% , the C_2 selectivities were 92 and 42% respectively. At 0.8% oxygen content in the methane feed the selectivity was 18% . A study on the oxidative coupling of methane over silver indicated that strongly bound atomic oxygen, formed by diffusion of dissolved oxygen to the silver surface, was responsible for the formation of C_2 product. Weakly bound atomic oxygen also can form C_2 hydrocarbons, but mainly it leads to complete oxidation.

A ceramic membrane reported by Hazbun [53, 54] comprised an impervious outer layer of mixed conducting zirconia (10% yttria, 89% ZrO_2 , and 1% TiO_2) on top of a porous inner layer of magnesia stabilized zirconia (87% ZrO_2 and 13% MgO) with catalyst inside. The conducting layer was doped with CeO_2 or TiO_2 to give electrical conducting character to the ceramic. This eliminated the need for an external circuit to provide an electron conducting path. For methane dimerization, oxygen was supplied to the shell side of the reactive two layer tubular membrane with methane gas within the tube. Temperatures were in the high range of $800\text{-}1,000^\circ\text{C}$, and depending upon process conditions conversions in the range of $10\text{-}50\%$ were achieved at selectivities higher than

50%. Paraffins predominated among the hydrocarbons products. With Li/MgO as catalyst the C₂ selectivity and yield were 50~60% and 20~25% respectively.

The yields of approximately 20% by Hazbun were respectable but not out of the ordinary. The selectivity was quite low, but the catalyst chosen may not have been optimal. Presumably the bulk gas reactions with oxygen were suppressed, and surface reactions to CO_x were responsible for the selectivities. This configuration appears promising and merits further study.

Cable *et al.* [92] reported a dense membrane reactor for oxidation reactions. The solid membranes comprised a gas-impervious, multi-phase mixture of an electric conductive material and an oxygen ion-conductive material and/or a mixed metal oxide of a perovskite structure. The reactor cells containing these membranes could also contain a catalyst in the first of the two zones separated by a membrane.

A different approach was taken by Omata *et al.* [93], who coated an impermeable (PbO/MgO) layer on the shell side of a 50nm porous alumina tube. Air was fed to the tube side, from which oxygen diffused through the porous support to the oxide layer. CH₄ was fed on the shell side, and C₂ products were withdrawn only on that side. No oxygen or nitrogen penetrated to the shell side. Selectivities higher than 97% were reported, but no conversions were stated. An approximate calculation based on data from the paper gives conversions below 1%. Temperatures were about 750°C.

It appears that CH₄ reacted with surface oxygen in this reactor, to form C₂ products. The oxide catalyst was replenished by diffusion of oxide ions through the lead oxide film. It is not clear whether the low conversions were due to a low activity catalyst, choice of processing conditions or limitations of oxygen transport through the lead oxide. Again, further study may be warranted of this configuration.

1.1.7.2 Porous Membrane Reactors for OCM

A recent study by Mouaddib *et al.*, [94] used yet another type of membrane reactor. A porous (125 - 300 μm pores) tube of SiO_2 - Al_2O_3 was packed with supported palladium silver oxide catalyst. CH_4 was fed on the tube side and O_2 on the shell side. The reactor was run at temperatures less than 300°C , so that only surface reaction took place. Very low conversions and selectivities were obtained, with yields typically below 1%, attributed chiefly to the choice of catalyst.

The advantages of this arrangement are that a high loading of an active catalyst can give higher conversions, the O_2 supply can be metered to be constant along the reactor tube through the porous walls (this avoids high oxygen partial pressures near the reactor entrance) and the arrangement is closest to existing technology. The disadvantages are that temperatures are increased to increase conversion, and the presence of oxygen in the bulk gas, although at a lower average level than in a conventional fixed bed reactor, may allow non-selective gas phase reactions to occur. In addition, oxygen may competitively chemisorb on active sites and react as molecular oxygen to CO_x . However, it is not possible to evaluate this reactor due to the low activity catalyst used by Mouaddib *et al.*, [94] and the C_2 yields were too low (<0.5%).

OCM on a porous alumina membrane reactor prepared by modifying porous alumina membranes with silica was studied by Santamaria and co-workers [50, 51] and C_2 selectivity higher than the conventional packed-bed reactor was obtained. Another study on OCM by catalyst packed-bed porous membrane reactor was done by Xu *et al.* [95]. An alumina membrane with pore size of 0.6 μm was used as support and doped with LiNO_3 - Sm_2O_3 mixture and calcined at 800°C . At 700°C the C_2 selectivity was 100% and CH_4 conversion was 3.6%.

1.1.7.3 Reactor Designs with Intermediate Product Removal

By using a simulated counter-current moving-bed chromatographic reactor (SCMCR), Tonkovich *et al.* [45] reported 50% C_2 yield for OCM with Sm_2O_3 as catalyst. A similar approach was taken by Jiang *et al.* [46] who developed a molecular sieve trap in the re-cycle loop of an electro-catalytic reactor-separator in order to accomplish product removal and improve process yields.

In the simulated counter-current moving bed chromatographic reactor (SCMCR) studied by Tonkovich *et al.*, [45] the methane conversion was significantly-increased by introducing intermediate stages of product removal through a moving bed chromatographic column. This reactor setup consisted of four reactor units maintained with a high ratio of methane to oxygen (50:1) and four separation columns to remove the C_2 hydrocarbons from the unreacted methane and oxygen. While this cyclic process seems attractive because of enhanced C_2 yields (40 to 50%), the energy requirements and complexity of the setup pose problems for commercialization. The methane coupling process must operate at high temperatures ($>750^\circ C$) while the adsorption of the desired products in the chromatography columns is favored at low temperatures ($< 200^\circ C$). Dautzenberg *et al.* [47] report that while the coupling reaction itself is exothermic (~ 66 Kcal/mole of C_2 s produced), the overall contribution of deep oxidation reactions makes the process even more exothermic (~ 123 Kcal/mole of C_2 s produced). Their study concludes that multi-tubular reactors of impractical dimensions would be required to control the heat transfer and avoid temperature runaways and that newer reactor designs are necessary for commercialization.

From the viewpoint of economics and industrial application, C_2 separation (either by cryogenic and adsorption technology) and methane recycle are attractive for OCM processes, such as GTG process developed by ARCO [96], the OXCO process by CSIRO

and BHP [82], and the Union Carbide Process [43]. This concept of product removal therefore holds promise for future directions for OCM technology.

In summary, some interesting catalytic membrane reactor configurations have been tried for methane dimerization. There exists much room for improvement, however, in both choice of catalyst and in engineering of the reactor design and operation. Control of the oxygen supply by use of a membrane may be the key to a successful methane coupling reactor. For the OCM technology to become commercially viable, C_2 yields have to be higher than the presently attainable levels of 20-25%. Although many metal-oxide catalysts that exhibit selectivity for the formation of C_2 hydrocarbons have been widely studied in fixed bed reactors, the higher CH_4/O_2 ratios required to minimize complete oxidation cause small CH_4 conversions and moderate C_2 yields [30,46]. The major goal of methane coupling research is to carry out the reaction at higher conversions, say 40-50 percent, while maintaining near total selectivity to C_2 -hydrocarbons, to avoid scrubbing CO_2 in the recycle stream.

1.2 Thermodynamic Studies: Evaluation of OCM Catalysts for Use in Membrane Reactors and of Operating Conditions for OCM.

Each of the three different configurations of the membrane reactors that were proposed to be studied in the course of this research imposed physical constraints on the choice of catalyst. In addition to the three membrane reactors, a conventional packed bed reactor would be studied with the same catalyst to compare with the membrane reactor's performance. This packed bed reactor and the porous membrane packed bed reactor required catalyst in pelletized form, with the pellet size determined by the surface area available and the pressure drop permissible in the packed bed. The porous catalytic membrane reactor, where the catalyst would be in the pores of the membrane required a catalyst synthesis technique that would involve precipitation of the solid catalyst from a solution, so that the membrane pores could be infiltrated with the catalyst solution. In the case of the dense membrane reactor, the catalyst would be deposited on the dense

membrane itself and hence the catalyst material should bind to the metal oxide material that constitutes the dense membrane. Hence, these additional factors had to be considered in selecting a catalyst for membrane reactor studies. We have used a thermodynamic analysis to define a basis for comparing the performance of various OCM catalysts reported in the literature that operated at different experimental conditions.

1.2.1 Maximum Theoretical Yield (Y^*)

The criterion that is normally employed to choose a catalyst is the yield of the favorable product that is produced by that catalyst. In this study, the C_2 yields reported for various catalysts in the literature were ratioed to a "theoretical maximum C_2 yield" to give an index of the efficiency of the catalyst.

The products observed in the high temperature catalytic activation of methane are mainly CO_2 , H_2 , C_2H_6 , C_2H_4 , CO , and H_2O . The maximum C_2 yields would be achieved if there were no formation of CO_x (that is if the C_2 hydrocarbon selectivity could go up to 100%). Since almost all the methane coupling experiments are carried out with excess of methane, we assume that there is no oxygen left in the product stream. A thermodynamic model based on minimization of the Gibbs Free Energy of the reaction system was developed to obtain equilibrium yields of the C_2 products, C_2H_4 and C_2H_6 .

Appendix A gives a detailed description of the thermodynamic model equations used to calculate the theoretical C_2 yields for the methane coupling reaction for a given set of operating conditions. The equilibrium composition of the methane oxidation system without CO and CO_2 formation provides us the upper limits of practically achievable C_2 yields. For example, if one is carrying out a methane coupling experiment at 1000K and 1 atm. with a methane to oxygen ratio of 8.0, the C_2 yield would never exceed 27.3%. Using the above equation by fixing the CO_x yield, we can also calculate the equilibrium composition at a certain CO_x yield for experimentally measured data and

show how much lower the experimental C_2 yield is compared with the maximum value at the same CO_x yield.

The maximum C_2 yield also provided a basis for the evaluation of catalysts prepared and designed for the methane coupling process. Studies of the performance of catalysts reported by different authors were carried out at various experimental conditions (temperature, pressure, methane oxygen ratio, amount of inerts added, and etc.). Reasonable evaluation of the catalyst should be based on the ratio of the C_2 yield of the catalyst to the maximum C_2 yield at the same conditions (Y/Y^*), and not solely on the absolute magnitude of C_2 yield or selectivity. Table 2.1.1-1 lists the performance of some typical catalysts and the maximum C_2 yields at their corresponding conditions.

It is clear from Table 2.1.1-1 that the C_2 yields achieved by most of the catalysts reported are only 30 to 50% (or less) of the maximum values, which suggests that thermodynamic limitations are not the reason for the C_2 yields experimentally obtained being less than 30 %.

This catalyst evaluation based on thermodynamic analysis presents only one facet of the multi-dimensional problem of the choice of a methane coupling catalyst. In addition to this criterion, traditional requirements on activity, selectivity, operating temperature, and longevity of the catalyst, and the particular reaction configuration etc., have to be all considered in selecting a catalyst.

1.2.2 Catalyst Chosen for OCM Studies: Sm_2O_3

For the studies on comparing the performance of porous membrane reactors with conventional co-feed reactors, Sm_2O_3 was chosen as the methane coupling catalyst. Apart

Table 2.1.1-1 Some Typical Catalyst and Their Performances

Catalysts	Authors	Temp.	CH ₄ /O ₂ Ratio	C ₂ Selectivity	C ₂ Yield (Y)	Y/Y* (%)
SrCe _{0.9} Yb _{0.1} O _{2.9} 5	Machida [62](1987)	750°C	2	60.1%	31.6%	31.6%
MnO/NaCl/TiO ₂	Feng- Chang [65](1989)	750°C	2.75	61%	26%	35.3%
Pb ₂ Mn ₂ Si ₂ O ₉ /Si O ₂	Thomas [97] (1988)	800°C	7.7	67.5%	20.3%	67.2%
Li NiO ₂	Kikhtyani n [98] (1987)	697°C	6	46.7%	12.1%	68.3%
Li/MgO	Lunsford [3] (1985)	720°C	2	50.3%	19.0%	19%
10%Li/ Sm ₂ O ₃	Otsuka [63] (1987)	750°C	2.5	57.0%	21.1%	23.4%
La/MgO	Choudary [49] (1989)	850°C	8.0	80.4%	16.2%	54%
Sm ₂ O ₃	Burch [99] (1987)	750°C	2.0	52.3%	7%	41.2%

from being an “efficient” catalyst with regard to the thermodynamic maximum theoretical yield analysis, Sm₂O₃ has further advantages over the other methane coupling catalysts. Being a single oxide, it is thermally stable and does not pose problems of compositional variation presented by mixed-metal oxide catalysts. Sm₂O₃ does not need a support as do the metal-on-metal oxide catalyst systems. Its activity toward methane coupling places it among the very efficient methane coupling catalysts. Further, very little catalyst deactivation was found to occur even after prolonged use under reaction conditions.

1.2.3 Equilibrium composition of CH₄-O₂ mixtures

Equilibrium compositions of CH₄-O₂ mixtures were calculated by the minimization of the total Gibbs free energy of the system. Figure 1-1 shows the equilibrium composition of CH₄-O₂ mixture as a function of temperature at a methane to oxygen ratio of 2:1. At temperatures higher than 650°C, the major thermodynamic reaction products are CO and H₂. This suggests that the oxidative conversion of methane to syn-gas is thermodynamically more favorable than to other products such as methanol, formaldehyde, and C₂ hydrocarbons. The concentration of the different products decreases in the following order:

Syn-gas (CO+H₂) > C₂ (C₂H₆, C₂H₄, or C₂H₂) > Oxygenates (HCOH, CH₃OH)

The above order explains why of the three routes, only syn-gas production from methane oxidation has shown promise for commercialization and less progress has been made in conversion of methane to methanol and formaldehyde than OCM. For catalyzed reactions, the yields of oxygenates are only few percent at most [100].

1.2.4 The effect of temperature on OCM

As shown in Figure 1-2, there are two optimum temperatures in the C₂H₆+C₂H₄ yield curve: 500°C and 950°C. Since no active low temperature catalyst has been developed so far, most of the OCM studies have been carried out at higher temperatures. The high optimal temperature (~950°C) is consistent with the observed value for methane conversion less than ~13% by Esktrom *et al.* [101]. This optimal temperature will shift to lower temperatures at higher methane conversions because the C₂ oxidation becomes more important at higher methane conversions.

Figure 1-1. Equilibrium composition of $\text{CH}_4\text{-O}_2$ mixture as a function of temperature at a methane to oxygen ratio of 2:1.

Although the product concentrations between the experimental and equilibrium values may differ by several orders of magnitude, the general trends of the temperature dependence of the relative amounts of C_2H_4 to C_2H_6 and CO to CO_2 are the same, as indicated by the C_2H_4/C_2H_6 and CO/CO_2 curves in Figure 1-2.

1.2.5 The effect of initial methane to oxygen ratio on OCM

Experimental results show that an increase of CH_4/O_2 always results in higher C_2 selectivity. This observation is shown by the thermodynamic analysis of OCM at $800^\circ C$ in Figure 1-3, where the relative amount of C_2 to CO_x increases with methane to oxygen ratio. This is the thermodynamic evidence for employing a membrane reactor, in which the CH_4/O_2 ratio is kept at higher values compared to conventional co-feed reactors.

1.2.6 Conditions favoring carbon formation

The issue of carbon formation in the OCM process is not extensively addressed in the literature. Thermodynamic analysis shows carbon could be formed at OCM conditions depending on the initial CH_4/O_2 ratio and composition (such as water vapor content) and temperature. In fact, carbon was observed by some of the researchers and some OCM catalysts also catalyze the cracking process of hydrocarbons, which is one of the sources for C_2 loss especially in the latter part of the reactor where oxygen is exhausted [70]. The local methane to oxygen ratio in the membrane reactor is much higher than that in a conventional reactor and carbon is more likely to be formed in this situation. Thus it would be necessary to find out the conditions, under which carbon may be formed or prevented.

Figure 1-2. Temperature dependence of relative amounts of C_2H_4 to C_2H_6 and CO to CO_2 .

Figure 1-3. Relative amounts of C_2 to CO_x with varying methane to oxygen ratio.

The dependence of equilibrium carbon mole fraction on temperature and initial methane to oxygen ratio is shown in Figure 1-4. Over a wide range of temperature and CH_4/O_2 ratios, carbon formation is thermodynamically favorable. High CH_4/O_2 ratio and low temperature favors carbon formation. Carbon formation could be reduced or prevented by co-feeding water vapor in the feed stream. From the kinetic point of view, the amount of carbon formed also depends on the nature of the surface of the catalyst and reactor wall and contact time of the reaction mixture with the solid surface.

1.2.7 Explosion conditions limiting OCM

Another limitation to C_2 yield is due to the maximum oxygen concentration imposed by the explosive limit of $\text{CH}_4\text{-O}_2$ mixtures [102] especially in the industrial process where the operation pressure is usually higher than in the lab-scale reactor and high dilution of the feed gas mixtures is unfavorable and causes more separation cost afterwards. Although the local oxygen to methane ratio is much less than the explosion limit on the reaction side of a membrane reactor, an explosion could occur if the membrane were to fail unexpectedly. According to the results from parametric studies (Chapter 7), the optimal overall ratio of oxygen to methane for membrane reactor is always higher than that for the co-feed reactor. There are no data available on explosion limits at higher temperatures and high pressures. Flammability diagrams for the methane-oxygen-nitrogen system at atmospheric pressure and 26°C are available in the literature. The explosion limits at higher temperatures can be calculated by the modified Burgess-Wheeler law [103] from low temperature explosion limits. The pressure and temperature of explosive mixture can be calculated by determining the equilibrium state of the initial gas mixture at constant internal energy and volume.

1.3 Kinetic Evidence Favoring Membrane Reactors

Theoretical studies of general parallel-series reaction systems (see Chapter 7. Mathematical Modeling), of which one case is the oxidative coupling of methane, suggest that the reaction order in oxygen for the desired reaction has to be lower than that for the undesired reactions for the membrane reactor to offer higher yield of the desired product. Therefore it is necessary to examine the reaction orders in oxygen in the kinetic expressions obtained for different OCM catalysts. Table 1-2 summarizes the reaction orders with respect to methane and oxygen in the rate expressions for C_2 and CH_4 formation reported in literature.

A compilation of the literature reports on kinetic studies on oxidative coupling of methane using various catalysts shows that, except for the data by Bartsch *et al.* [104], the reaction order in oxygen for C_2 formation is always lower than that for CO_x formation. In conclusion, for most catalysts, the apparent reaction order for oxygen in the deep oxidation reaction is higher than in the coupling reaction. This means that modes of contact which maintain a low oxygen concentration throughout the reactor should favor the desired versus the undesired reaction [79].

Catalytic OCM is a complex process and involves both surface and gas phase reactions, which can be generalized as four steps: a) Methyl radical generation on catalyst surface; b) Methyl radical coupling in gas phase; c) methyl radical oxidation; and d) C_2 oxidation. The ultimate C_2 yield is determined by the magnitude and relative values of all the reaction rates for the four steps, which depend mainly on the catalyst and

Figure 1-4. Dependence of equilibrium carbon mole fraction on temperature and initial methane to oxygen ratio.

Table 1-2 Apparent reaction orders in methane and oxygen for C_2 and CO_x formations

Catalysts	Temp. (K)		C ₂ formation		CO _x formation		
			CH ₄	O ₂	CH ₄	O ₂	
	923~1073		1.04/ 1.16	1.78/ 1.62	-0.53/ -0.95	3.70/ 1.33	Lane and Wolf, 1988 [105]
Li/MgO	900~1050		0.75	-0.2~0.1	-0.1	0.8	Mirodatos and Martin, 1988 [106]
Li/BeO	953		1.0	0.3~0.5	0	1.0	Doi <i>et al</i> , 1988 [107]
9.7%Li/NiTiO ₃	923		1.0	0.0	0.5	0.3	Miro <i>et al</i> , 1990 [108]
	973		1.1	0.0	0.3	0.6	
	1023		1.2	0.2	0.4	0.7	
1.6%Na/NiTiO ₃	973		1.2	-0.3	0.6	0.5	
	1023		1.1	0.1	0.5	1.2	
	1073		1.0	0.4	0.6	1.0	
LaAlO ₃	983	m/o>4	0.9-1.0	0.5~1.2	0.1~0.7	1.4~1.7	Tagawa and Imai, 1988 [109]
		m/o<4	1.7-1.9	-0.8~0.7	0.7~0.9	0.5~1.2	
PbO/Al ₂ O ₃	1013		0.8	1.1	0.4	1.5	Hinsen <i>et al</i> , 1985 [110]
	953~1073		1.07	1.4	0.6~1.0	2.0~0.34	Carreiro <i>et al</i> , 1988 [111]
PbO/MgO	1023		0.9	0	0.4	0.7	Asami <i>et al</i> , 1987 [112]
Sb ₂ O ₄	1023~1073		0.9	0.5	0.4	0.8	Lo <i>et al</i> , 1988 [113]
5%K-Sb ₂ O ₄			0.6	0.2	0.1	0.8	
33%K-Sb ₂ O ₄			1.1	1.0	0.2	1.0	
Sb-SiO ₂			0.8	0.7	0	0.7	
5%K-Sb/SiO ₂			1.0	0.4	0.5	0.5	
K-Bi ₂ O ₃ /Al ₂ O ₃			2	1	0.3	1	
Li/MgO	873~1023		0~1.34	0~1.34	0~0.67	0.67~ 1.34	Tung and Lobban, 1992 [115]
Ce/Li/Al ₂ O ₃	1023		2	1.2	0	0.6	Bartsch <i>et al</i> , 1991 [104]

CH_4/O_2 in addition to temperature and pressure. A good catalyst will be the one that catalyzes step a) but not steps c) or d). Note here that high methyl radical concentration is always beneficial for high C_2 selectivity as well as methane conversion because the coupling reaction is of second order with respect to methyl radical and the methyl oxidation reaction is less likely of being of order 2 or more.

An increase in CH_4/O_2 ratio (equivalent to decreasing O_2 partial pressure while keeping methane partial pressure constant) will definitely suppress the undesired reactions c) and d), in which oxygen is involved. However, at high methane to oxygen ratio, oxygen is usually the limiting reactant and methane conversion decreases as CH_4/O_2 increases. As a result, there is always an upper limit of CH_4/O_2 ratio in order to achieve highest C_2 yield.

In spite of the extensive studies carried out on oxidative coupling of methane in the past decade, the best reported C_2 yields are still in the vicinity of 25~30% no matter what kind of catalyst and experimental conditions are used. Since many changes in catalyst, its composition, and conventional reactor process parameters have been unsuccessful in finding a route to high C_2 yield, the research for yield improvements in OCM began to cool down in the last few years. Many researchers believe that there is an inherent single-pass C_2 limit (ca. 30%) for OCM regardless of the reaction conditions and catalysts. This conclusion was made based on conventional packed-bed reactor operation in co-feed mode. The C_2 limitation could be overcome if one can increase the CH_4/O_2 ratio while maintaining a significantly high methane conversion. This can be done by feeding oxygen successively to the reaction system to keep a high 'local' (or 'instant' depending on the type of reactor used) methane to oxygen ratio and, at the same time, maintain a reasonable methane conversion by adjusting the total amount of oxygen introduced to the system. Only under this circumstance could both selectivity and conversion be increased at the same time and the C_2 yield could be improved. The above

concept could be realized by using staged feeding reactors or membrane reactors of specific configurations.

1.3.1 The Research Approach of this Study: Oxygen Metering

Experimental proof of improvements in hydrocarbon selectivity by control of feed policy were shown conclusively by Choudary *et al.* [49] who studied fixed bed reactors with staged/distributed oxygen feed. This approach was also taken in the work of Lafarga *et al.* [50] and Coronas *et al.* [51] through the use of modified alumina membrane reactors, and in the theoretical work of Reyes *et al.* [48]. We had also used this approach of controlling the flow of oxygen through porous inorganic membrane reactors to study the effects of oxygen metering on the OCM reaction. Shell-and-tube type membrane reactors were employed in our studies, where the catalyst was packed in porous Vycor membrane tubes. Oxygen flowed from the shell-side to the tube-side through the porous membrane at a rate controlled by the applied pressure differential between the shell and the tube.

A modified porous Vycor reactor could withstand the high temperatures required for the methane coupling reaction and also provide a steady oxygen flux, allowing better distribution of the reactant gases over the catalyst bed, than the conventional plug flow reactor, thereby maintaining a low gas phase concentration at the catalyst site. Experimental results using modified alumina membranes to control the oxygen flow reported by Coronas *et al.*, [51a] and Lafarga *et al.* [50] and our results were in agreement that improvements in C_2 selectivity were realized in the OCM reactions carried out under metered flow in membrane reactors. Our studies [116] were the first to report the use of porous Vycor membranes to enable a precise control of the oxygen delivery along the

length of the catalyst bed. Experimental studies of oxidative coupling of methane in dense membrane reactors were also investigated.

Chapter 2. Material Synthesis and Characterization

2.1 Membrane Selection and Membrane Modification.

Several materials that are traditionally used as membranes were investigated for use in the membrane reactors that were employed in our studies of the oxidative coupling of methane. To build a membrane reactor on a lab-scale, the membrane should enable very slow diffusive fluxes, since the physical size of the equipment and the instrumentation needed to control the gas flows (mass flow controllers) could operate in the range of only 1 to ≈ 500 ml/min. Therefore, we needed to find membranes that would provide diffusive fluxes that would produce flows of approximately 10 ml/min.

For studying the oxidative coupling of methane, it was proposed to regulate the flow of oxygen through the use of membranes in membrane reactors. Two types of membranes were of interest, dense membranes, which would simultaneously allow separation as well as regulation, by allowing only oxygen to diffuse through the material, and porous membranes, whose sole function would be to regulate the flow of oxygen. At the time of starting this project there were no commercial sources for dense membranes so experiments were undertaken to investigate synthesis of dense membranes. Commercial porous membranes were available, but these could not be employed directly for the high temperature applications that OCM requires. Hence, another major effort in this research was in identifying possible candidates and modifying them for use at high temperatures in membrane reactors.

2.2 Dense Membranes

Oxygen conducting dense membranes can be fabricated either by compaction of the oxygen conducting materials to form densified pellets or tubes, or by filling the pores in porous membranes with oxygen conducting materials. To modify the commercially available porous membranes, perovskite type oxides have been used because of their

electrical conductivity and oxygen permeation properties. After densification of the membrane by closing the pores of the membrane completely, the dense membrane should be preferentially permeable to oxygen transfer. For the dense membrane to operate without any external electrical circuit and to aid in oxygen (anion) transfer, the densification material should also be electrically conducting. Perovskite-type oxides are therefore good candidate materials for densification of porous membranes.

Two approaches were followed in developing dense membranes. The first was to fill the pores of commercially available porous materials with oxygen conducting perovskites. This effort involved developing techniques to synthesize perovskite materials in various forms (gels, solutions, particulates etc.) and deposit them in a variety of porous inorganic membranes. α -alumina, γ -alumina, and zirconia were commercially available as inorganic membranes that were useable for high temperature operation and were tried as supports for dense membrane synthesis by perovskite deposition. Appendix B1 discusses the various synthesis techniques that were employed to prepare the perovskite materials. Appendix B2 details the results of those experiments where each of the inorganic membrane materials was tried as a support for depositing the perovskite. Perovskite deposition in the pores of the inorganic membranes was achieved, as evidenced by XRD and changes in permeation rates of various gases through these modified membranes. Appendix B3 details the results from the permeation measurements on the modified inorganic membranes.

As discussed in Appendix B, complete pore closure was not achieved and dense membranes could not be made by the solution deposition technique. Research efforts involving particulate deposition in porous supports were relatively more successful. In this technique, nanometer size particulates of a buffer layer were deposited on porous supports before depositing the nanoparticles of the oxygen conducting perovskite. Appendix H describes the principle of cavitation and the operation of the Microfluidizer[®], an instrument available in our laboratory that was employed to synthesize oxygen conducting materials as nanoparticles. In this set of experiments,

pore closure was achieved, but the dense membranes thus formed did not remain stable at temperatures required for oxygen transport through the perovskite material. These experiments are discussed in detail in Section 5.

The second avenue of dense membrane synthesis research dealt with synthesizing disks of pure perovskites that could be used to conduct oxygen. This approach was successful in producing dense membrane disks of perovskites. Appendix B4 describes the synthesis and dense disk preparation techniques. Results on oxygen conduction through these dense perovskite disks are also presented in Appendix B4. During the latter part of this research program, under a collaborative effort with Argonne National Laboratory, oxygen conducting dense membrane tubes were used in membrane reactors and oxidative coupling of methane was studied.

2.3 Porous Membranes

Several commercially available porous materials have been tried for use as membranes in a porous membrane reactor. Among the ceramic materials, α -alumina, and zirconia were available as tubular membranes with pore diameters of 2000 Angstroms and 500 Angstroms respectively. These membranes are radially asymmetric and the labeled pore diameters are seen only in the top-layer of the membrane. Typically, the thickness of the top-layer ranges from 2μ to 10μ . The top-layer is built up on several (3 or 4) intermediate layers and a support layer which are all made up of increasingly larger grains of alumina. Due to the small thickness of the top layer and the 200-2000 Angstrom pore diameters in the top layer of the commercially available membranes, relatively high gas fluxes are obtained for small values of pressure drop across the membranes. γ -alumina membranes are available with a top layer pore size of 40 Angstroms but were unstable at temperatures greater than 650°C . Even the ceramic membranes modified by perovskite deposition as described in Appendix A permitted very high flow rates of gases across the membrane tubes. However, pore modification and stabilization of γ -alumina membranes was successful as described in Chapter 6.

Another successful candidate for use as a membrane material was porous Vycor[®] (glass) membrane. Porous Vycor (commercial name "thirsty glass") is the intermediate porous leached form of the basic consolidated (non-porous) Vycor. Corning Inc. markets this porous Vycor with a product designation as 'glass number 7930'. Physical and chemical properties of porous Vycor are found in Appendix C1. Unlike the alumina and zirconia membranes, these Vycor membranes have the same pore structure over the entire membrane cross section. This provides a longer path for passage of gases across the membrane and would be advantageous in membrane reactor configurations where we deposit the catalyst inside the membrane pores, since we can achieve higher catalyst loading inside the porous structure of the membrane. The longer diffusion paths also lower the permeance values in these membranes which might be beneficial in controlling the intermixing of gases in our lab-scale membrane reactors operating at very low flow rates.

One disadvantage of using porous Vycor is that thermal treatments cause a change in the pore structure of the material, which results in a change in gas permeance through the material. Data have been collected to monitor this change in gas permeance through porous Vycor membranes as a function of temperature. Since Vycor is essentially a glass, it tends to "flow" at the higher temperatures. The real issue for the use of a Vycor membrane as a high temperature membrane material needed for the reaction study of oxidative coupling of methane is the stability of the permeance value at the reaction temperature over the duration of the experiment. To test this stability of permeance, experiments have been performed wherein Vycor membranes were treated at 850°C over extended periods of time. All measurements were made at room temperature, after the subsequent high temperature treatment for a specified amount of time at the set temperature.

2.3.1 Gas Permeation through porous Vycor

Room temperature permeance of nitrogen gas through porous Vycor was measured to be 4.5×10^{-8} mol/s.m².Pa. Results from the studies on steady state gas permeance at room temperature through porous Vycor membranes after having been pre-treated at a high temperature over a prolonged time period are presented in Figure 2-1. At a pre-temperature of 850°C, the permeance of the nitrogen gas through the membrane at room temperature increased over a 48 hour period and reached a steady-state value of 1.5×10^{-7} mol/s.m².Pa.. For higher treatment temperatures, steady state permeance was achieved within 48 hours as well, although the amount of gas permeance changed with increasing treatment temperature.

These studies indicate that it is important to attain a steady state with respect to structure stabilization for measuring the permeance of gases through the material. Typically it takes about 24-48 hours for the porous structure of Vycor to stabilize and for the gas permeance to reach a steady state. Since a typical experimental run would last between 24 and 48 hours, and methane coupling would be studied in the temperature range 650°C-850°C, all the Vycor membranes were treated at 900°C for 48 hours before use in the experimental studies. This procedure, hereafter referred to as "pre-treatment" procedure, was employed in all characterization and experimental studies with porous Vycor membranes.

The changes in gas permeance through the porous Vycor membranes were systematically monitored as a function of the pre-treatment temperature. Literature reports of permeance of helium gas [117] indicate that there is a sharp drop in the value of the gas permeance at pre-treatment temperatures greater than 850°C. Figure 2-2 shows the values of nitrogen gas permeance measured as a function of the pre-treatment temperature. All the permeation measurements were made at room temperature. Gas permeance is relatively unchanged for pre-treatment temperatures less than 850°C. Between 850°C and 1000°C, there is a sharp decrease in the value of nitrogen permeability through porous Vycor.

Figure 2-1. Steady State Permeance of Nitrogen Gas through thermally treated porous Vycor.

At 1200°C , the material becomes totally dense and gas permeance drops to zero. These results are in very good agreement with literature reports on the permeance of helium gas through porous Vycor [117] which indicate that there is a sharp drop in the value of the gas permeance at pre-treatment temperatures greater than 850°C . These results were utilized in devising a fabrication procedure for preparing a porous Vycor membrane module discussed in a later section.

While all the above permeance measurements were made at room temperature, it should be recognized that the results could be applied to high temperature operation. The experiments conclusively showed that once structural stabilization was achieved, there was no further change in permeance irrespective of how long the higher temperature was maintained. This fact was also borne out by experiments where gas permeance was continuously monitored at high temperatures in the 750°C - 850°C range and no changes in the permeability were observed. Thus, the membrane modules made by using porous Vycor that had been pre-treated would reproducibly deliver the same amount of gas flow across the porous membrane over several cycles of use.

2.3.2 Shrinkage measurements on porous Vycor

Along with the permeability measurements on pretreated Vycor membrane tubes discussed above, shrinkage measurements were also performed. The structural change that caused the lowered gas permeance through the material causes axial and radial shrinkage of the membrane tube. Figure C3 (in Appendix C3) shows that the linear shrinkage is about 2.5% at 850°C and about 6.35% at 1000°C . These results are in close agreement with the data reported by Shelekhin *et al.* [117]. The transition temperature regime of 850 - 1000°C presents the maximum increase in shrinkage of the material. These data were utilized in deciding on the physical dimensions of the membrane module.

Figure 2-2. Room temperature measurements of nitrogen gas permeance through porous Vycor membrane as a function of the pre-treatment temperature.

2.3.3 Pore size measurements on porous Vycor

Pore size measurements were made on porous Vycor using nitrogen physisorption and BET surface area/pore volume measurements on an analytical pore size instrumentation-Autosorb-1c (Quantachrome Co.). Appendix C4 describes the technique employed for obtaining the pore-size distributions in thermally pre-treated porous Vycor. Figure C-4 in Appendix C4 shows the pore size distribution for the Vycor that underwent thermal treatment at 900°C.

A very sharp pore size distribution, with the peak position at 45 Angstroms, was observed. No detectable change was observed in this pore size distribution before and after the thermal pre-treatments, but the pore volume decreased from 0.25 cc/gm to 0.025 cc/gm, indicating that only total collapse of an increasingly larger number of pores occurred with increasing temperature. These data are in very good agreement with those of Shelekhin *et al.* [117], who reported a systematic study of BET surface areas and pore volumes as a function of the pre-treatment temperature. They observed identical dependence of pore volume (cc/gm) and BET surface area (m^2/gm) with the pre-treatment temperature and concluded that this was possible only if there was no change in the pore diameter with pre-treatment temperature. The uniform pore size throughout the porous section of the membrane ensured that there was uniformity in the radial distribution of permeating gas in the membrane module.

The fact that gas permeance through the membrane could be adjusted by controlled calcination which resulted in controlled pore closure was especially beneficial to our study and helped in devising a reliable membrane module fabrication procedure. Appendix C5 describes in detail the methodology and procedure followed in preparing a porous Vycor membrane module for use in the shell-and-tube type membrane reactor. These porous Vycor membrane reactors were employed in studies on oxidative coupling of methane and are discussed in Section 3.

2.3.4 Gas flow control through applied pressure differential across the porous Vycor membranes

Figure 2-3 shows the permeate flows of helium and oxygen as a function of the applied pressure differential across the porous Vycor membrane. These measurements were made at room temperature. Pure oxygen was fed on the shell side and helium gas flowed on the tube side. Gas permeate flow was found to vary linearly with the applied pressure differential and this allowed a precise control on the amount of oxygen delivered to the tube side. Helium and oxygen permeate flows differ by a factor of $2\sqrt{2}$. This difference in the values of permeate flow of helium and oxygen is in accordance with the square root of the ratio of their molecular weights ($Z_{\text{He}}=4$; $Z_{\text{oxygen}}=32$) thereby confirming that the flow through the pores of the Vycor was restricted to the Knudsen regime.

Figure 2-4 shows the results where oxygen permeate flow was monitored at room temperature, 200°C and 400°C across the membrane. The pressure driven permeate flow showed linear dependence with applied pressure differential with increasing pressure drop across the membrane. It was also observed in these experiments that the value of permeance (and the flow across the membrane) did not change over extended time periods.

The absolute value of gas (oxygen) permeate flow through the porous Vycor membranes was considerably lower than those used in commercial setups. In industrial applications, this lower permeance might be a problem in terms of productivity. However, in our lab-scale experimental setup where the methane flow rates were comparatively small, a low oxygen permeance through the membrane in conjunction with lower flow rates allowed conditions where transfer of reaction gases through the membrane from shell to tube side could be metered.

Figure 2-3. Gas permeate flow across the porous Vycor membrane as a function of the applied pressure differential.

Figure 2-4. Oxygen permeate flow across the porous Vycor membrane with pressure differential, as a function of temperature.

Chapter 3. Tube-and-shell Reactor Studies with Porous Vycor Membranes

3.1 Membrane Reactor Description

The objective of this experimental study was to investigate methane coupling under conditions of metered oxygen flow. To achieve this metering of oxygen flow, porous Vycor membranes were employed. By applying a pressure differential across the wall of the porous membrane, oxygen flow could be regulated across the membrane wall. The heterogeneous catalysis of oxidative coupling of methane required a solid catalyst to activate the reaction. The reactant gases had to be contacted over the catalyst bed at high operating temperatures ($> 750^{\circ}\text{C}$).

A reactor design that met the above specifications was the shell-and-tube reactor where the porous Vycor membrane would serve as the “tube”. The solid catalyst was packed inside the tube. Methane gas was flowed inside the tube while the oxygen flow was metered across the porous membrane tube wall. The “shell” side of the reactor contained oxygen at high pressure such that the pressure difference between the high pressure shell side and the low pressure tube side would control the flow of oxygen across the membrane wall. The constant pore size all through the porous section minimized the radial and axial inhomogenities in the amounts of oxygen permeate flow along the porous section.

While the porous Vycor membranes can withstand the pressure differences and allow small gas fluxes to permeate across the membrane wall, the challenge is to fabricate a membrane module that can withstand the high temperatures ($>750^{\circ}\text{C}$) needed for methane coupling. A general description of the membrane module fabrication procedure is provided here and a step-by-step fabrication procedure is presented in Appendix D.

A composite five-sectional Vycor-Quartz membrane module served as the membrane module of the shell-and-tube reactor. The membrane module consisted of a well defined central porous region with a permeability to nitrogen of 20,000 Barrer,

porosity minimized sections on either side of the central porous region with a permeability of about 200 Barrer, and two 10 mm O.D. quartz tube end sections. The membrane module fabrication was devised based on the results of material characterization of porous Vycor (i.e. linear and axial shrinkage, permeation and pore diameter measurements.)

A 30 cm long porous Vycor tube was first pre-treated at 900°C for 24 hours. The porosity minimized sections were then made from this pre-treated tube by subjecting a length of approximately 10 cm from each of the two ends to an additional thermal treatment at 1100°C for 24 hours. The Vycor tube was then cut so that the porous section was centered. The two end sections were then glass-welded onto two non-porous quartz tubes of 10 mm O.D. and of equal length to make up a five-sectional membrane module with a total length of 52 cm. Figure 3-1 shows a cross sectional view of the five-sectional membrane module. The lengths of the porous section could be varied just by subjecting different lengths of the Vycor material at the higher temperatures, but in a typical membrane module, the porous section was about 10 cm and the porosity reduced sections were about 7 cm. The transition region between the porous central region and the porosity reduced Vycor was generally limited to less than 1 cm.

The membrane module thus fabricated was housed inside a quartz-lined stainless steel tube to make up the membrane reactor. The porous membrane reactor was a shell-and-tube type reactor with the catalyst packed inside the membrane tube. The membrane module which served as the tube for the membrane reactor, or the quartz non-porous tube which was used in the conventional co-feed reactor, was fitted into the reactor by using Kalrez® O-rings (located outside the heated zone) to provide leak-tight seals between the tube and the shell. The catalyst, mixed with quartz chips, was confined to the porous region of the membrane (or the non-porous quartz) tube and was packed in the annular region between a 3mm OD quartz thermowell and the 7 mm ID Vycor membrane tube. Figure 3-2 shows a cross-sectional view of the annular catalyst bed in the membrane reactor. The rest of the tube side volume was packed with quartz chips for the

Figure 3-1. Schematic of the Vycor membrane module cross section.

Figure 3-2. Cross Section View of the Packed Bed in the Vycor Membrane Reactor.

purpose of reducing the reactor volume and thus minimizing non-selective gas phase reactions.

3.2 Catalyst Characterization

Fig. 3-3 shows that several conventional methane coupling catalysts have been investigated for their activity toward methane coupling in our experimental studies. Those investigated included the traditional alkali and alkaline earth metals on oxide supports such as Li/MgO and La/MgO that were used by Lobban *et al.* [115], Santamaria *et al.* [50], and Lunsford *et al.* [57], and single oxides like Sm_2O_3 , as well as the complex oxides and perovskites like $\text{SrCe}_x\text{Yb}_{(1-x)}\text{O}_3$, $\text{Sr}_{(1-x)}\text{La}_x\text{FeO}_3$ and $\text{Sr}_{(1-x)}\text{La}_x\text{CoO}_3$. While the metal on oxide support catalysts Li/MgO and La/MgO posed problems with deactivation and volatilization, the perovskite type complex oxides exhibited poor hydrocarbon selectivity. Section 5 on perovskite materials discusses in detail the activity of these perovskites toward oxidative coupling of methane. These studies were conducted in conventional co-feed, packed bed reactors, since the objective of this study was to compare the catalytic efficiencies of the oxides toward methane coupling. Sm_2O_3 outperformed the complex oxide catalysts by exhibiting both higher methane conversions as well as higher hydrocarbon selectivities.

Apart from being the most commonly used methane coupling catalyst [1,17], and commercially available in high purity grade, Sm_2O_3 also showed no deactivation and loss in selectivity for more than 100 hours on stream. Since the experimental thrust of this portion of the study was to compare the reactor performance of the membrane reactor and the conventional co-feed reactor, the use of a simple, stable oxide obviated the problems of catalyst dispersion (as in Li/MgO [22-26]) or concentration inhomogeneities (as in mixed oxide catalysts like SrCeYbO_3 [11,15]). Sm_2O_3 (particle size $\sim 1\text{-}2\ \mu$) was purchased from Aldrich Co. (Cat.# 22,867-2). The catalyst powder was mixed with quartz chips and packed in the annular space between a quartz thermowell and the membrane tube.

Catalytic Activity Tests for Oxidative Coupling of Methane Quartz Tube Reactor, 12 cm Catalyst Bed

- 1gm $\text{Sr}_{0.8}\text{La}_{0.2}\text{FeO}_3$ Catalyst
- ✚ 1 gm Sm_2O_3 Catalyst
- 1 gm $\text{SrCe}_{0.8}\text{Yb}_{0.2}\text{O}_3$

Figure 3-3. Conversion-Selectivity plot for the various catalysts to assess their methane coupling activity.

Several studies in the literature showed that samarium oxide catalyst was a highly active and selective for the oxidative coupling of methane [1-13]. Since commercially obtained Sm_2O_3 powder was used in our work for catalyzing the methane coupling reaction, it was therefore studied for phase changes and modifications using XRD. The XRD pattern of the fresh samarium oxide (as purchased), without any pre-treatment presented in Figure 3-4 showed both the cubic and the monoclinic phases of Sm_2O_3 . A sample of samarium oxide which was used for the oxidative coupling of methane reaction in the Vycor membrane reactor, for a total run time of 70 hours, was analyzed by XRD and the XRD peak spectrum is presented in Figure 3-5. The maximum temperature measured during the reaction was 810°C . A comparison of the XRD peak patterns showed a reduction in intensity of the diffraction peaks corresponding to the monoclinic phase and an increase in the peak intensity corresponding to the cubic phase of Sm_2O_3 . This indicated that there was a greater quantity of the cubic phase of samarium oxide after reaction. The fraction of monoclinic did not appear to decrease, suggesting that the transformation of the monoclinic into the cubic was unlikely. A likely possibility was that the fresh samarium oxide contained an amorphous phase which transformed into the cubic phase at the high temperatures of the methane coupling reaction. The formation of the cubic phase was beneficial, since studies in the literature indicated that the cubic phase of Sm_2O_3 was the more active form for oxidative coupling of methane [15,16] and is the thermodynamically stable phase at 810°C .

3.3 Description of the Apparatus

Through the utilization of multiple heat controlled zones, we were able to achieve acceptable isothermal conditions over the porous membrane-catalytic bed section of the membrane reactor. Since the feed gases had to be heated to the reaction

Figure 3-4. XRD spectrum of fresh Samarium oxide showing the presence of both the cubic and monoclinic phases.

Figure 3-5. XRD Spectrum of the samarium oxide sample after 70 hours on stream in the methane coupling reaction.

temperatures before contacting the catalyst, it was necessary to pre-heat the feed gases. The first heating zone on the top of the reactor served as the pre-heating zone. By monitoring the temperature profile along the centerline of the reactor at the top of the catalyst bed, the pre-stage heater temperature was regulated to provide adequate heating of the feed gases. The pre-heater was a cylindrical, 3 inches long, 110 Volt, ceramic heater and was purchased from Thermcraft Inc. The temperature of the pre-heater was controlled by an Eurotherm PID controller.

The main heater for the reaction zone was similar to the pre-heater, but 6 inches in length. The temperature of the main heater was controlled independent of the pre-heater and the post-heater by a Eurotherm PID controller. The catalyst bed (10 to 12 cm long) was centrally located in the main heater section, which was 15 cm long. While the Eurotherm controller regulated the heat supply and maintained a set-point temperature, the actual temperature at the heart of the catalyst bed was measured by the thermocouple that slid inside the thermal well.

To maintain a uniform and flat temperature profile in the main heater zone, a 3 inch long, cylindrical post-heater was positioned below the main heater. The temperature on the post-heater was controlled by its own Eurotherm PID controller and its set-point temperature was dictated by the uniformity of the temperature profile provided in the bottom part of the main heater. The temperature of the post heater had to be adjusted whenever changes were made in the reaction temperature (main heater temperature) or the feed flow rates.

Figure 3-6 shows the three heater setup positioned around the shell-and-tube membrane reactor. A 2 inch thick insulating foam encased the cylindrical heaters that surrounded the shell-and-tube reactor. The axial temperature profile in the packed bed shell-and-tube membrane reactor is shown in Figure 3-7.

The quartz thermowell was positioned along the axis of the membrane tube and allowed a sliding thermocouple to profile the temperature along the reactor bed. The thermowell not only helped to minimize oxygen starvation at the core of the catalyst bed, but also allowed the sliding thermocouple to profile the axial temperature while the reactor was operating at the higher temperature. Figure 3-7 shows the temperature profile along the axis of the shell-and-tube membrane reactor. An isothermal profile, with a deviation of less than 1.2 % (a variation of 10°C at 850°C set point temperature) was obtained over the central 12 cm zone of the membrane reactor. Cooling water lines around the reactor body on either side of the heat zone maintained the O-ring fittings at lower temperatures.

3.4 Experimental Setup

Methane gas diluted with five times as much helium was fed to the tube side. Pure oxygen was fed to the shell side and its flow into the tube was controlled by the pressure differential between the shell and the tube sides, set by using back pressure controllers. The feed flow was controlled using Mass Flow Controllers (Models 5850 series C/5851 series E) which were purchased from Brooks Instruments. The argon gas flow was regulated through an independent MFC and was mixed with either the tube side or the shell side effluent in a spiral-tube mixer before being sent to the GC for analysis. A schematic of the experimental setup is shown in Figure 3-8. The reactor piping was 1/8 inch SS tubing except at the entrances and exits to the shell-and-tube reactor which were 1/4 inch SS. The entire post reactor piping, including the GC sampling loop, was insulated and kept at 150°C.

Figure 3-6. Schematic of the shell and tube reactor setup showing the three heating zones.

Figure 3-7. Axial temperature profile down the reactor length in the Vycor membrane reactor.

Figure 3-8. Schematic of the shell-and-tube reactor setup used for porous Vycor membrane studies.

The shell and tube reactor housing the membrane or a quartz tube was brought up to reaction temperature at a rate of $2^{\circ}\text{C}/\text{min}$, under flowing helium. Once the operating temperature was reached, the shell side was pressurized with pure oxygen. Oxygen permeate flow into the tube side was monitored by measuring the O_2 content in the tube side effluent through GC/MS analysis. The methane flow was then introduced by mixing with helium flowing on the tube side and both the tube and shell side exit flows were analyzed for product concentrations. In the case of the co-feed quartz tube reactor, first the oxygen, and then the methane, were mixed in appropriate amounts with the helium gas and were co-fed into the tube side and the tube side exit flow was analyzed.

The effluent flows from the reactor were analyzed by an on-line GC-MS system (HP5890 Series II-GC, HP 5971-MSD). A Poraplot-Q megabore column (0.53 mm column ID, purchased from Alltech Co.) was used to resolve the CH_4 , C_2H_4 , C_2H_6 , and CO_2 peaks, while the Ar, CO and O_2 peaks that co-eluted were resolved by the Mass selective detector. Figure 3-9(a) shows the GC peak spectrum with all the peaks labeled with the corresponding species. The components of the first peak were further resolved by the Mass Selective Detector as shown in Figure 3-9(b), and quantification of individual components was carried out. Concentrations of CH_4 , O_2 , C_2H_4 , C_2H_6 , CO and CO_2 were computed by calibrating against a standard gas mixture containing all the product gases in known quantities, and CH_4 conversions and C_2 ($\text{C}_2\text{H}_4 + \text{C}_2\text{H}_6$) selectivities and yields and the carbon balance were calculated.

3.5 Methane Coupling Studies

3.5.1 Blank Reactor Experiments

In the blank reactor experiments, the reactor was filled with quartz chips and equivalent flow and temperature conditions were maintained as in the catalyst packed

(a)

(b)

Figure 3-9. (a) GC peak spectrum using Poraplot-Q showing individual, separated peaks for CH_4 , CO_2 , C_2H_4 and C_2H_6 . (b) Mass Spectrometer spectrum showing resolved Ar ($Z=40$), CO ($Z=28$) and O_2 ($Z=32$) peaks obtained from the unresolved GC spectrum peak.

membrane and co-feed quartz tube reactors. For both the blank reactor runs as well as the catalytic runs, closure was obtained on the carbon balances between 96% and 102%. For the experimental conditions in Table 1, methane conversions in the blank runs were in the range of 7-9% for the Vycor membrane reactor, and 4-5% for the blank runs in the quartz non-porous reactor at 800°C, as shown in Figure 3-10. At higher reactant flow rates, the blank conversions were much lower (2-3%).

3.5.2 Comparison of porous Vycor membrane reactor with non-porous quartz reactor

The aim of the experimental work was to study a 40Å pore size porous Vycor membrane reactor and compare its performance with a quartz tube non-porous packed bed reactor. The study of a non-porous quartz tube packed bed reactor was carried out to establish a base line case. A comparison of the reactor performance of the two reactors was made on the basis of the amount of methane converted, C₂ selectivities and the total C₂ yields. These comparisons were made while maintaining equivalent flow and temperature conditions for the two reactor systems.

Comparisons of reactor performance were made between the porous Vycor membrane reactors and the conventional non-porous packed bed reactors packed with the Sm₂O₃ catalyst and operating under equivalent experimental conditions of the reaction temperature, catalyst loading, and feed flow rates (Table 3-1). The CH₄ conversion, C₂ selectivity and C₂ yield were calculated based on outlet compositions according to the following definitions.

$$\text{CH}_4 \text{ Conversion} = \frac{[\text{moles of (CO}_2 + \text{CO)}] + 2[\text{moles of (C}_2\text{H}_4 + \text{C}_2\text{H}_6)]}{[\text{moles of (CO}_2 + \text{CO)}] + 2[\text{moles of (C}_2\text{H}_4 + \text{C}_2\text{H}_6)] + [\text{moles of CH}_4]}$$

Figure 3-10. Methane conversion in a Vycor membrane reactor filled with quartz chips.
(Blank Reactor Run).

$$\text{C}_2 \text{ Selectivity} = \frac{2[\text{moles of } (\text{C}_2\text{H}_4 + \text{C}_2\text{H}_6)]}{[\text{moles of } (\text{CO}_2 + \text{CO})] + 2[\text{moles of } (\text{C}_2\text{H}_4 + \text{C}_2\text{H}_6)]}$$

$$\text{C}_2 \text{ Yield} = \frac{2[\text{moles of } (\text{C}_2\text{H}_4 + \text{C}_2\text{H}_6)]}{[\text{moles of } (\text{CO}_2 + \text{CO})] + 2[\text{moles of } (\text{C}_2\text{H}_4 + \text{C}_2\text{H}_6)] + [\text{moles of } \text{CH}_4]}$$

Figure 3-11 compares the C₂ selectivities in the porous Vycor membrane reactor and the quartz non-porous reactor operated at the same contact time of 0.86 seconds. C₂ selectivities were consistently higher in the Vycor membrane reactor over the temperature range 700°C-800°C, compared to the non-porous quartz tube reactor. With increasing temperatures, the non-selective gas phase methane conversion to CO_x products increased. Hence, the C₂ selectivity decreased as the reaction temperature increased over 750°C. The overall C₂ yields were about the same in both reactor configurations as shown in Figure 3-12.

Total methane conversions for the two reactor systems are shown in Figure 3-13. The higher conversions seen for the quartz tube fixed bed reactor were mainly caused by the deep oxidation to CO_x products as seen by the low values of C₂ selectivity at the corresponding temperatures for this reactor configuration. Figure 3-14 shows the conversion versus selectivity plot that compares the performance of the Vycor membrane reactor with that of the co-feed non-porous reactor. At the same level of conversion, membrane reactors produce higher C₂ selectivity compared to non-porous co-feed reactors. Since the membrane reactor had inherently lower methane conversions at the higher operating temperatures, for this comparison of conversion vs. selectivity, the data for the quartz tube non-porous reactor correspond to much lower operating temperatures than the membrane reactors.

TABLE 3-1. Experimental Conditions for Vycor membrane reactors

Experimental Parameter	Vycor Membrane Reactor	Quartz Non-porous Reactor
He flow	200 ml/min	200 ml/min
CH ₄ flow	40 ml/min	40 ml/min
O ₂ flow	20 ml/min (permeate)	20 ml/min
Shell side pressure	65 psi	-
Catalyst bed length	12 cm	12 cm
Catalyst (Sm ₂ O ₃) loading	2.4 gms	2.4 gms

For both the Vycor membrane reactor and as the quartz non-porous reactor, Figure 3-14 shows that higher selectivities corresponded to the high methane conversion data. This was because the lower methane conversion data were obtained at temperatures less than 700°C where the C₂ production was essentially negligible.

The fact that metering the oxygen flow into flowing methane in the catalyst bed enhances the C₂ selectivity is further supported if only the products from the tube side effluent are considered in computing the hydrocarbon selectivity. Although this computation does not necessarily claim that membrane reactors outperform the

Figure 3-11. Comparison of C₂ selectivities from porous Vycor membrane reactor and co-feed, non-porous quartz reactor.

Figure 3-12. Comparison of C_2 yields from porous Vycor membrane reactor and co-feed, non-porous quartz reactor.

Figure 3-13. Comparison of CH₄ conversions from porous Vycor membrane reactor and co-feed, non-porous quartz reactor.

(d)

Figure 3-14. Conversion vs. selectivity plot indicating the performance of porous Vycor membrane reactor and the non-porous quartz tube reactor. The different conversions were obtained at different reaction temperatures.

conventional co-feed reactor, it does strengthen the case for oxygen metering, since it is only on the tube side of the membrane reactor that oxygen is metered. Figure 3-15 shows the data on CH_4 conversion and C_2 selectivity by considering the performance of only the tube side of the membrane reactor. On this conversion-selectivity plot, the Vycor membrane tube exhibits much higher C_2 selectivity at lower methane conversions than the combined shell-and-tube reactor. These data therefore strengthen the argument of C_2 selectivity enhancements due to oxygen feed control. Naturally, any methane that escapes to the shell side, which contains no catalyst, is converted into CO_2 . Figure 3-16 shows that the C_2 selectivity is significantly higher in the membrane tube when compared to its non-porous quartz tube counterpart, both reactors being run at the same inlet feed conditions. This indicates that modifications in membrane reactors that minimize losses to shell side, such as dense membrane reactors that selectively permeate oxygen, hold promise for further advancements in the field of OCM technology.

3.5.3 Effect of Oxygen Concentration

These studies were aimed at exploring the effects of conducting the methane coupling experiments under conditions where the oxygen conversion was far from complete. Since we were investigating a reactor system that operated on the principle of metering the oxygen supply, it was necessary to study the reaction under conditions where the oxygen was present in excess.

Figure 3-17 shows a comparison of the methane conversion with reaction temperature from porous Vycor membrane reactors under oxygen rich and oxygen lean environments, run at equivalent flow conditions and at a methane to oxygen ratio of 0.5.

Figure 3-15. Comparison of tube side effluent in Vycor membrane reactor with the overall effluent (tube+shell) of the Vycor membrane reactor and the quartz tube non-porous reactor.

Figure 3-16. Variation of Tube side C₂ Selectivity with reaction temperature in comparison with the product selectivity in the non-porous quartz tube reactor.

Oxygen lean conditions resulted in almost complete conversion of oxygen, limiting the amount of methane that could be converted to between 40% and 60%. Though this limitation on methane conversion was overcome under oxygen rich conditions, a decline in C_2 selectivity was observed as shown in Figure 3-18. These results indicate that metering the oxygen flow through porous membrane reactors is beneficial to the methane coupling reaction when most of the oxygen supplied to the catalyst bed is used up before exiting the reactor. This was ascertained by carrying out similar experiments at various methane to oxygen ratios as shown in Table 3-2.

3.5.4 Effect of Methane to Oxygen Ratios

For comparing the performance of the Vycor membrane reactor with the co-feed reactor, experimental studies of the oxidative coupling of methane employed a methane to oxygen ratio of 2.0. Literature studies indicated that a conventional packed bed, co-feed reactor provided maximum hydrocarbon yields while operating at a CH_4/O_2 ratio of around 2.0 [3,14,41]. A higher ratio would decrease overall methane conversion, while a lower than 2.0 ratio would reduce C_2 selectivity. In the case of the Vycor membrane reactors also, a CH_4/O_2 ratio of 2.0 maximized the C_2 yields as can be seen from the

Table 3-2. Performance of Vycor membrane reactor under O_2 rich conditions.

CH_4/O_2	CH_4 Conversion	O_2 Conversion	C_2 Selectivity	C_2 Yield
2.0	20%-25%	40%-90%	30%-20%	5%-10%
1.0	10%-30%	30%-60%	20%-15%	2%-5%
0.5	90%-100%	40%-50%	10%-2%	2%-5%

Figure 3-17. CH₄ conversion and C₂ selectivity in Vycor membrane reactors operated under O₂ rich and O₂ lean conditions.

plots of CH_4 and O_2 conversions, C_2 selectivity and yield shown in Figures 3-18 and 3-19 for the reaction temperatures of 720°C and 830°C respectively. These experiments were carried out by first setting the shell side oxygen pressure to a fixed value so that the oxygen permeate flow was constant. Methane flow on the tube side was then varied to obtain the CH_4/O_2 ratio for each set of data. These results show that C_2 yields were optimal at a CH_4/O_2 ratio of 2.0. The same result was obtained at other operating temperatures between 650°C and 850°C . Since both the membrane reactor and the non-porous reactor exhibit optimum hydrocarbon yields at a methane to oxygen ratio of 2.0, feed flow rates used in the reactor performance comparison experiments were based on a CH_4/O_2 ratio of 2.0 to avoid undue advantage to either reactor type. For the porous Vycor membrane reactor, the total oxygen permeate flow from the shell into the tube was obtained from GC analysis before introducing the appropriate amount of methane on the tube side. For the quartz non-porous reactor, oxygen that was co-fed along with helium was analyzed in the GC and appropriate amounts of methane were pre-mixed and co-fed.

3.5.5 Effect of Metering Methane Flow

Since oxygen was the competing reactant for methane coupling as well as for methane deep oxidation, most of the experimental work involved metering oxygen flow through the porous membrane tube of the reactor. Due to the higher reactivity of C_2 hydrocarbons over methane with oxygen, metering in oxygen flow was counter-productive in the lower part of the catalyst bed and detrimental to C_2 selectivity.

Figure 3-18. Effect of changing CH_4/O_2 ratio on the performance parameters during oxidative coupling of methane in Vycor membrane reactor at a reaction temperature of 720°C .

Figure 3-19. Effect of changing CH₄/O₂ ratio on the performance parameters during the oxidative coupling of methane in Vycor membrane reactor at a reaction temperature of 830°C.

The following experiments were performed to test the effect of metering methane flow into a flowing stream of oxygen. Since the C_2 products that were produced in the front sections of the reactor bed were susceptible to oxidation, these experiments of metered methane flow were aimed at improving the overall C_2 selectivity. The Vycor membrane reactor was run in a configuration where pure methane was fed to the shell side while oxygen mixed with helium diluent was fed to the tube side (catalyst packed inside the tube). Methane permeate flow for methane metering was equal to the oxygen permeate flow for the oxygen metering experiments and all these experiments were run at an overall methane to oxygen ratio of 2.0.

Figure 3-20 compares the methane conversions and Figure 3-21 compares the C_2 selectivities in these experiments with those of oxygen metering at equivalent flow conditions. An improvement in the overall C_2 selectivities was obtained as expected, as compared to the earlier studies that were run with oxygen on the shell side. Higher methane conversions, however, lower the selectivities, resulting in very low C_2 yields.

3.6 Results and Discussion

Experimental studies of oxidative coupling of methane were conducted with porous Vycor membrane reactors and conventional non-porous packed bed reactors operating under equivalent conditions. C_2 selectivities were consistently higher in the

Figure 3-20. Methane conversions under conditions of oxygen metering and methane metering.

Figure 3-21. C₂ selectivities in Vycor membrane reactors under O₂ and CH₄ metering

Vycor membrane reactor over the temperature range 700°C-800°C, compared to the non-porous quartz tube reactor. With increasing temperature, the non-selective gas phase methane conversion to CO_x products increased. Hence the C_2 selectivity decreased as the reaction temperature went up. The overall C_2 yields were about the same in both reactor configurations. The membrane reactor has an overall C_2 yield of 11%, while the quartz tube fixed bed reactor has 10% C_2 yield at the same conditions. At the same level of conversion, the membrane reactors afforded higher C_2 selectivity. The higher C_2 selectivity in the membrane reactor shows that for the methane coupling reaction, regulating the supply of oxygen along the length of the packed bed is beneficial for the C_2 product formation.

Since, in the membrane reactor, methane combustion was accomplished under limited oxygen supply, the level of methane conversion was not as high as in the co-fed quartz tube reactor. Higher methane conversions require greater contact times in porous membrane reactors. For the same feed flow conditions, longer contact times translate into larger reactor volumes. A larger bed cross-section is not desired as that would increase methane and hydrocarbon losses to the non-selective reactions on the shell side. This problem has been addressed by employing a relatively long catalyst bed (10-12 cm) and fast sweep gas rates.

By using a thermowell and quartz chips to dilute the catalyst bed, hot spots and thermal runaways were minimized. The catalyst powder (1-2 μ) was well dispersed among the 60-80 mesh size quartz chips. The temperature profile shown in Figure 3-7 remained unchanged when the feed gases (methane and oxygen) were introduced, indicating that the exothermicity of the reaction was adequately handled and the heat generated during the reaction was efficiently dispersed.

Use of the 40Å pore diameter, 1.5 mm thick walled Vycor membrane enabled a more uniform cross-flow of oxygen (flow across the membrane wall) down the catalyst

bed as compared to the work of Coronas *et al.* [51a] whose modified alumina membrane reactor setup had a steep axial gradient of oxygen flow. The low value of gas permeance through the Vycor membrane implied that a high pressure differential (60 psi) was needed to obtain a permeate flow of about 10 ml/min of oxygen. Since the quartz chip dilution of the catalyst bed created only 1-2 psi upstream head-pressure, a reasonably constant pressure differential was maintained along the bed length, which meant a uniform distribution of oxygen permeate along the bed length.

A comparison of the experimental results with the methane coupling results reported by Coronas *et al.* [51a], who used modified porous alumina membranes in a similar shell-and-tube configuration, shows agreement with the trends of higher selectivity and lower conversion in membrane reactors. At the same $W/F=0.01$ g-min/cc and methane conversions, our experiments showed a higher C_2 than that reported by Coronas *et al.* [51a,b]. This was probably due to a better control of metering the oxygen flow axially down the catalyst bed in our system, provided by the uniform pressure driven flow through 40Å pores of the membrane. Their study also concluded that regulating the supply of oxygen along the length of the packed bed provided higher C_2 selectivity in the membrane reactor as compared to a fixed bed reactor with comparable C_2 yields for both the reactor configurations. Our results confirm this conclusion.

Though it is arguable that the uniform oxygen permeate flow along the reactor length could have been detrimental to C_2 selectivity at the lower end of the reaction zone, where there is a higher concentration of C_2 s, our modeling studies indicated that imposing a gradation in permeance down the catalyst bed was not expected to cause significant improvements in the overall C_2 selectivity. Recent work reported by Coronas *et al.* [51b] indicates that though improvements were discernible, the overall improvements in C_2 selectivity and C_2 yield were no more than 1-2 percentage points.

The fact that metering the oxygen flow into flowing methane in the catalyst bed enhances the C_2 selectivity can further be substantiated if only the products from the tube

side effluent are considered in computing the hydrocarbon selectivity. Although this computation does not necessarily claim that membrane reactors outperform the conventional co-feed reactor, it does strengthen the case for oxygen metering, since it is only on the tube side of the membrane reactor that oxygen is metered. On the conversion-selectivity plot, the Vycor membrane tube exhibits much higher C_2 selectivity at lower methane conversions than the combined shell-and-tube reactor. These data therefore strengthen the argument of C_2 selectivity enhancements due to oxygen metering because oxygen metering occurs on the tube side and mainly deep oxidation of methane occurs in the oxygen rich shell side. This indicates that modifications in membrane reactors that minimize losses to shell side, such as dense membrane reactors that selectively permeate oxygen, hold promise for further advancements in the field of OCM technology.

Although our studies do not show marked improvements in the total C_2 yields in Vycor membrane reactors, they clearly indicate that improvements were obtained in C_2 selectivity through oxygen metering in membrane reactors. These results warrant further investigations into improvements in reactor designs that could result in commercialization of the OCM technology. One such research avenue is dense membrane reactors where the dense membranes would prevent methane and hydrocarbon losses to the shell side, while at the same time permit significant flux of oxygen across the membrane.

Chapter 4. The Oxidative Coupling Of Methane In Porous Ceramic Radial-Flow Catalytic Membrane Reactor

Many different reactor configurations have been tried [47], with some of the more recent being the use of membrane reactors to provide a distributed oxygen feed [79, 116] to lower the oxygen partial pressure in the reactor, thus favoring C_2 formation over CO_x formation, and the removal of the C_2 products following the reactor, as in the gas-recycle electrocatalytic reactor-separator [46] and in the countercurrent moving-bed chromatographic reactor [45]. These efforts, while promising, have not yet achieved an industrially attractive process for direct conversion of methane to C_2 products.

The concept of the radial-flow catalytic membrane reactor is based on the simple idea that if one conducts methane coupling within the fine pores of an inorganic membrane where the flow is in the Knudsen regime, then this type of reactor design will ensure a minimum degree of further contact of the products, ethylene and ethane, with the oxygenated surface (Fig. 4-1). It is known that the carbon oxide non-selective products mainly result from the interaction of ethane and ethylene with an oxygenated surface. The consequence of the radial-flow configuration is that flow through a really fine pore, having for example a diameter of $0.02\ \mu\text{m}$, reduces the possibility for the C_2 species to react with any oxygenated surface, by controlling the contact time of the gases with the catalyst. At the same time, the radial-flow geometry can provide a large cross-flow area within a reasonable reactor volume, so that scale-up to industrial gas flow rates is possible.

It is known that oxygen reacts rapidly with nearly all metal oxide surfaces to provide activated oxygen. It is this species that is responsible for activating methane, but it is the same species that forms carbon oxides when it reacts with ethane or ethylene. The radial-flow membrane reactor ensures that the methane that enters the porous structure is activated; however, ideally, the surface oxygenated species should be deposited only in the fine membrane structure, as shown in Fig. 4-1, and not deeper in the porous membrane support structure, to ensure that no ethane and ethylene can react with the oxygenated catalyst to

form non-selective products. In addition, the gas passing through the fine pores will be in the Knudsen diffusion regime, in which gas-gas molecular interactions occur less often than gas-wall (catalyst) interactions. This will tend to suppress non-selective gas phase reactions, and ensure maximum contact of the reactants with the catalyst surface. The smaller the pore diameter, the more effective should be the contact. This structure should lead to a higher activity compared to a conventional packed bed of catalyst.

Figure 4-1. Conceptual schematic of methane coupling within an individual pore in a radial-flow membrane reactor

The essential idea of the radial-flow fine pore membrane reactor is, therefore, to allow the methane to react with the oxygenated surface to form methyl radicals, and then to get the methyl radicals away from an oxygenated surface as rapidly as possible. Thus, the catalyst deposition is exceptionally important. The fine membrane structure where the methane co-mixed with oxygen flows into the pore must be homogeneously coated with the active catalyst on the pore walls. Little catalyst should be located within the transition or meso-pore structure of the support. In this way, the methyl radicals are formed by the oxygenated surface and the high flux of materials rapidly removes the radicals and ethane/ethylene product from this non-selective surface, and expansion into the mesoporous structure, containing no catalyst, results in the removal of the C_2 products without over oxidation.

The present chapter reports the initial experiments in the radial-flow catalytic membrane reactor. A range of fine pore diameters was covered, to illustrate the effects of pore size. Permeation experiments were run to confirm that gas transport was in the Knudsen regime. Catalytic experiments were carried out to demonstrate the concepts mentioned above, and comparisons to conventional fixed bed reactors showed the promise of the new membrane reactor configuration for methane coupling.

4.1 Experimental

The complete reactor assembly was constructed by joining a long cylindrical piece of nonporous Al_2O_3 tubing to a shorter membrane piece of porous alumina. The porous material consisted of one of several different α -alumina supports of 12–15 μm pore diameters with membrane top layers as given in Table 4.1. The top layers were located on the inner diameter of the porous tubes. The manufacture of the entire reactor tube was intended to create a reactor assembly large enough to place the active catalyst within the heated reaction zone of the heater.

The catalytic porous membrane reactor consisted of a porous Al_2O_3 tube containing an active Sm_2O_3 catalyst. The active oxide catalyst was deposited by flowing a deionised water solution with 20 wt. % dissolved samarium nitrate ($(\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O})$, F. W. 444.46, Aldrich) through the porous section. For each deposition cycle, 25 ml of the solution was pulled through the porous section using a vacuum on the shell side to force the solution to flow from the tube to the shell side. The reactor assembly was then placed in a temperature-programmable oven at 80°C for 4 hrs., then ramped to 120°C for 4 hrs. and heated to a final calcination temperature of 850°C for 4 hrs. All heating and cooling ramps were performed at 8°C/minute. The active cubic phase of Sm_2O_3 was maintained throughout the porous reactor experiments. The weight of catalyst deposited was determined by weighing the total reactor assembly before and after each catalyst deposition, after calcination. An average of six deposition and calcination cycles was required to obtain the approximately 100 mg of catalyst used in the experiments. SEM, XRD and EDX analyses were used to characterize

the reactor and catalyst.

Table 4.1. Experimental conditions for the radial-flow catalytic membrane reactor

<u>Operating conditions</u>	
Temperature (°C)	700 - 850
Feed composition	CH ₄ : O ₂ : He = 2 : 1 : 10
Flow rate (cc/min)	182 - 1820
Catalyst weight (mg of Sm ₂ O ₃)	□100
<u>Membrane characteristics</u>	
Support materials	α-Al ₂ O ₃
Toplayer thickness (μm)	30
<u>Dimensions (mm)</u>	
Inner diameter	7
Outer diameter	10
Length	26
<u>Top layer pore diameters (μm)</u>	
α-Al ₂ O ₃	5.0, 2.0, 0.5, 0.2
ZrO ₂	0.05, 0.02 (3 tubes)

The reactors were enclosed within a leak-free quartz tube outer shell (see Fig. 4-2). Swagelock fittings were sealed to the quartz tube using o-rings, which were cooled during reaction using forced air streams, so that the reactor apparatus could be connected to stainless-steel feed and product lines. The porous tube reactor apparatus was designed to minimize the free volume within the enclosed outer quartz tube shell while simultaneously minimizing the pressure drop through the apparatus due to flow restrictions. Quartz tubes were placed directly downstream and below the reactor and on the shell side. A movable K-type thermocouple, sealed at the top with a septum, was placed within the reactor and was

covered with a quartz tube sheath. This setup was modified slightly for the nonporous packed bed experiments. The feed gases, an ultra high purity O_2 , ultra high purity methane and helium diluent (Matheson) underwent pressure reduction and their flows were controlled using calibrated mass flow meters and measured by rotameters. Pressure transducers, accurate to 0.01 psi, were mounted directly at the feed inlet and outlet. The inlet pressure readings helped to identify pinhole leaks in the glaze seal between the porous and nonporous tubes, as the inlet pressure would then slowly decrease. A gas sampling Hewlett-Packard Series II Gas Chromatograph with a thermal conductivity detector was used to analyze the product gases. The experimental conditions are given in Table 4.1.

Figure 4-2. Membrane reactor configuration

Permeation experiments were performed at ambient temperature on the reactor tubes before and after catalyst deposition, and on the reactor tubes before and after reaction. The permeation studies tested the integrity of the glaze welds and helped to determine the existing flow regime of the gases through the porous tubes.

Two packed bed reactors were studied using the crushed catalyst-deposited porous section of one of the porous tube reactors for packing material. The first packed-bed reactor consisted of only the 60/80 mesh size material of the crushed porous tube reactor, to try to keep a uniform mesh size packing. Only a small amount (8.5 mg) of this material could be recovered, however, and so a second packed bed reactor was investigated using additional smaller mesh size fractions of the crushed porous tube, resulting in 27.3 mg of catalyst.

4.2 Results and discussion

Preliminary theoretical calculations on the fresh (unreacted) membrane, applying the dusty-gas model at 800°C, indicated that the flux in the 5.0 μm membrane should be 53% viscous and 47% Knudsen diffusion. For the membranes of pore size 0.5 μm and lower, transport was expected to be in the transition regime with less than 10% being contributed by viscous flow, and for the 0.02 μm membrane transport was predicted to be completely in the Knudsen regime. Fig. 4-3 shows the results of the permeation studies on the membranes after catalyst deposition, and it is clear that all except the 5.0 μm membrane were in the Knudsen regime, suggesting that catalyst had been deposited into the fine membrane structure and had resulted in lower permeation through the membranes.

Before the methane coupling experiments were performed with the active catalyst, blank reactor runs with the undeposited porous tube reactor were made to determine the reactivity of the set-up without catalyst. At the lowest flow rates (highest residence times) the methane conversion was less than 4% for all pore sizes. The stability of the Sm_2O_3 catalyst was investigated on some of the reactor tubes over a period of time. For the 0.5 μm and 2.0 μm pore diameter reactors, the catalyst did not substantially deactivate, with only the methane conversion decreasing by 1-2% over six days continuous operation. The 0.02 μm pore diameter reactors # 2 and #3 showed increasing total C_2 selectivities with time on-stream, and only minor catalyst deactivation, with the methane conversions remaining stable. A final steady-state was reached for these reactors in which the total C_2 selectivity stopped increasing (reactor #1 developed a pin-hole leak and could not be investigated further). The

Figure 4-1. Results from helium permeation experiments

reason for the different behavior of the 0.02 μm reactors is not well understood, but it may be related to grain growth within the fine pore structure.

A comparison of the performance of some of the membrane reactors is shown in Fig. 4-4, which is a plot of conversion against selectivity. The different conversions for each reactor were obtained by varying the feed gas flow rates. The calculations of CH_4 conversion and C_2 selectivity were based on the product compositions as determined from GC analysis, and are given by

$$X_{\text{CH}_4} = \frac{\text{carbon in C}_2 \text{ and CO}_x \text{ in product stream}}{\text{carbon in C}_2, \text{CH}_4 \text{ and CO}_x \text{ in product stream}} - (100\%)$$

$$S_{\text{CH}_4} = \frac{\text{carbon in C}_2 \text{ in product stream}}{\text{carbon in C}_2 \text{ and CO}_x \text{ in product stream}} - (100\%)$$

As shown in Fig. 4-4, with one exception, similar reactivity behavior was observed for the different pore size reactors. Slightly higher methane conversions were observed with lower C_2 selectivity in the higher catalyst loaded 5.0 μm reactor. The exception was the 0.02 μm reactor #1, which gave worse performance than the other reactors. Attempts to repeat the runs with this reactor were thwarted when it developed a pinhole leak, so a second reactor was synthesized. The results from this reactor changed with time as noted above, and the final steady-state performance was considerably better than the other membrane reactors. At this stage, consistency of the reactor tubes and reproducibility of the synthesis procedure were questioned, so a third 0.02 μm pore size reactor was constructed, and results from this reactor were comparable to those from the other pore size reactors, and lay between those of reactor #1 and reactor #2.

Figure 4-4. Conversion/selectivity plot for comparison of different pore size membrane reactor

To understand the difference in reactor performance of the three 0.02 μm pore diameter reactors, energy dispersive x-ray digital mapping (EDX) was used to characterize the three reactors. Using this technique, it was possible to qualitatively observe differences

in the location of deposited catalyst within the membrane. A cross-section of each of the three 0.02 μm reactors was used to perform an elemental mapping on samarium. Space precludes a detailed presentation of the results, which will be forthcoming. In summary, reactor #2 showed an even deposition of the catalyst within the membrane and intermediate layer with a decreasing concentration gradient into the support. In contrast, reactor #1 and reactor #3 were observed to have distinct high catalyst intensity lines at the outermost edge of their respective toplayers. An hypothesis which is consistent with the observations would be that for reactors #1 and #3 a significant amount of methane was converted to C_2 at the edge of the toplayer, and the product gases then diffused into the catalytically active toplayer where further oxidation to CO_x took place. In reactor #2, the conversion of methane to C_2 products took place only gradually within the toplayer, where the residence time for complete oxidation was much reduced. Hence, only reactor #2 approximated the ideal catalyst deposition, shown schematically in Fig. 4-1.

Fig. 4-5 shows the performance of the membrane reactors compared to packed beds of crushed catalytically-impregnated 0.02 μm membrane material, to remove differences in surface area and catalyst loading. In all cases the membrane reactors exceeded the performance of the packed bed reactors. In particular the C_2 selectivity for the two packed bed configurations was substantially lower than the selectivities from the membrane reactors.

Figure 4-5. Conversion/selectivity of membrane reactors and packed-bed reactors

4.3 Summary

The radial-flow catalytic membrane reactor studies clearly demonstrate that those reactors having the smallest pore sizes, which were coated with the active catalyst with reasonably good homogeneity through the fine membrane, outperformed all other reactors studied. These small-pore reactors were also most clearly in the Knudsen flow regime. The distribution of catalyst appears to be very important, as evidenced by the very different performance of the three 0.02 μm reactors. This supports the hypothesis that improved yield to C₂ products can be achieved by preventing contact of the products with oxygenated surfaces.

Chapter 5. Dense Membrane Reactors

One of the proposed areas of research was the investigation of dense membrane reactors. Dense membranes would allow selective passage of oxygen gas to the reaction zone, thus eliminating methane loss through the pores encountered in the porous membrane reactors. Oxygen conducting perovskites are good candidates for use in dense membrane reactors since they have very good high temperature stability and can withstand the pressure differences across the membrane wall at the high temperatures present during methane coupling. A wide variety of perovskites have been synthesized and characterized in this research for the preparation of dense membranes.

5.1 Dense membrane research objectives

The objectives of the dense membrane research conducted in this project were two-fold. One research avenue dealt with identifying and synthesizing oxygen conducting dense materials. Membrane reactors made using these oxygen conducting materials as dense membranes would then be used to study the oxidative coupling of methane. These dense membrane reactors would thus complement and present an improvement over the porous Vycor membrane reactors that were extensively studied during this project and discussed in Section 3. Dense membranes would allow metering of pure oxygen by separating oxygen from the air present on one side of the membrane, and at the same time, prevent any losses of methane or the hydrocarbons from the catalyst-bed side of the membrane reactor.

Although dense membranes can control the delivery of oxygen to the reaction system and there is no product loss from the membrane, the molecular oxygen has to get into the gas phase before meeting the catalyst, and gas phase C_2 oxidation still can not be completely eliminated. If a catalytic dense membrane (both an oxygen conductor and a methane coupling catalyst) were employed, the presence of gas phase molecular oxygen

in the gas phase could be avoided by controlling the oxygen flux such that it would match the OCM reaction on the surface of the catalyst.

The second research avenue therefore aimed at looking for materials that would not only conduct oxygen, but which were also catalytically active for methane coupling. Such dense membranes when used in the membrane reactors might significantly change the methane coupling chemistry by combining oxygen separation, oxygen transfer and oxidative coupling of methane, all occurring sequentially in one pass. By inducing the methane coupling reaction on the dense membrane material, it could be possible to accomplish methane activation through oxygen species other than molecular oxygen, such as oxygen anion, lattice oxygen or atomic oxygen [22].

5.2 Oxygen conducting materials: perovskites

Dense membranes can be made of oxygen-conductive ceramics. Most of the oxygen ion conductors have a perfect or distorted fluorite (CaF_2) structure (e.g. ZrO_2 , ThO_2 , CeO_2 , and Bi_2O_3), pyrochlore ($\text{A}_2\text{B}_2\text{O}_7$) structure, scheelite (CaWO_4) structure, or perovskite (CaTiO_3) structure (ABO_3), [119]. Complex oxides of rare earth materials that have a perovskite structure are frequently referred to as “Perovskite materials” or “Perovskites”.

The unique crystal structure of a perovskite allows the lattice oxygen to migrate inside the crystal through a hopping mechanism along the vacancies present in the lattice. Oxygen conducting perovskites typically have an $\text{ABO}_{3-\delta}$ type of structure where the A site can be substituted by a large cation and the B site can be substituted by a much smaller cation. This can induce charge imbalances as well as vacancies in the structure, especially when the charges on the substituting ions are lower than that of the host cation. While the stoichiometric amount of oxygen makes the oxide formula ABO_3 , the decrement by δ comes about because of oxygen mobility in the lattice induced by

temperatures greater than 800°C or by ion substitution. Perovskites of rare earths like Sr, La, Ce and Yb, in combination with group VIII elements like Fe and Co are known to permit oxygen conduction through their bulk. Literature reports also suggest that the oxygen conducted through these materials is not molecular oxygen, but rather, a charged or neutral ion [22]. Several perovskites have been synthesized using a variety of preparation techniques and were characterized for information on their structure, oxygen conductivity and chemical reactivity. Research efforts on the synthesis and characterization of these perovskites are discussed next.

5.2.1 Perovskite synthesis

The oxygen conducting perovskite, $\text{Sr}_{0.8}\text{La}_{0.2}\text{FeO}_3$, was synthesized by the following techniques:

1. The mixed solid oxide process.
2. The conventional solution precipitation technique
3. The sol-gel technique using ethylene glycol.
4. The cavitation technique using a Microfluidizer®.

A variety of perovskites of different elemental substitutions as well as varying extents of substitution were prepared using the above techniques. Details on the specific techniques are presented in the Appendices. Appendix B describes the synthesis of perovskites of the series $\text{La}_{(1-x)}\text{Sr}_x\text{FeO}_{3-\delta}$ by solution precipitation technique as well as the sol-gel technique and the ethylene glycol sol-gel technique. Appendix H describes the Microfluidizer technique for synthesizing perovskite materials.

5.2.2 The mixed solid oxide process

The mixed solid oxide process consists of the decomposition of precursor compounds, generally the nitrates containing the desired metal ion in air or oxygen. An intimate mixture of the nitrates is added in amounts corresponding to the relative contributions to the complex oxide. The solid mixture is then calcined at high temperatures (flashed) to cause a solid-state reaction where the nitrates are converted to the oxide and due to the extreme temperatures, the complex oxide were formed. Compositional homogeneity and phase purity are not very high in this synthesis technique and the solution processes described below were the main synthesis routes followed for preparing these perovskite-type oxides. The solution techniques involve intimate mixing of the metal ions in the solution state and allow synthesis at low temperature which results in high surface areas and more uniform compositions of the final product.

5.2.3 Solution co-precipitation method

This was a conventional technique where the nitrates of the metals constituting the complex oxide were brought into solution. A precipitating agent was added to a solution containing the precursor compounds. The homogeneity and the degree of atomic mixing of the metal ions in the precipitates depended on the solubility products of the compounds involved. Water was the most commonly used solvent, but depending on the value of the solubility product of the nitrate, organic solvents such as iso-propanol, ethanol, or other organic solvents were also used. Once a solution of all the nitrates in the required molal quantities to form an aqueous solution was formed, a precipitating solution was added drop-wise, under constant stirring. Typically, NH_4OH was the commonly used precipitate, since it was easy to decompose the NH_4NO_3 to obtain the complex metal hydroxide, which was then converted into the oxide by calcination at higher temperatures. Several perovskites of the family $\text{Sr}_x\text{La}_{(1-x)}\text{FeO}_3$ ($0 < x < 1$), and $\text{La}_{(1-x)}\text{Sr}_x\text{FeO}_3$ were synthesized using this technique. Appendix B1.1 details the solution

precipitation technique as well as the compositional variation and properties of some of the synthesized perovskites. Figure 5-1 shows that the perovskite prepared by solution precipitation technique and subjected to 590°C calcination produces a material with a high degree of phase impurity but contaminated with a second phase at 32.5 2θ . Figure 5-2 shows that the perovskite structure appears only at a calcination temperature of 800°C. The material calcined at 800°C still showed several reflections for separate non-perovskite phases.

5.2.4 Sol-gel technique

This is also a solution based technique, but instead of a solution, an amorphous gel of the pre-cursor nitrates was synthesized in ethylene glycol. Gelation occurred as the nitrate mixture in ethylene glycol was warmed to temperatures above 200°C, under constant stirring. The gel was then dried and calcined to form the complex oxide. This technique, termed the “Ethylene Glycol Technique”, produced complex oxides of very good compositional homogeneity and phase purity and was the main method used to synthesize the perovskites during this research. Appendix B1.1 describes the detailed procedure followed in the ethylene glycol technique to prepare the perovskites. The XRD pattern presented in Figure 5-3 shows that the material synthesized using the ethylene glycol technique has good phase purity and exhibits the perovskite structure for a calcination temperature of 590°C. However, when this material was calcined at 800°C, some non-perovskite phases appear, suggesting that the apparently pure perovskite phase resulting from the 590°C calcination actually contained some amorphous material.

5.2.5 Cavitation technique (Microfluidizer synthesis)

Perovskite synthesis in the Microfluidizer was accomplished by hydrodynamic cavitation [120,121] which produces nanometer size particles of the perovskite. Details of the cavitation technique and the principle of operation of the Microfluidizer are discussed in Appendix H. KOH and NH₄OH were used as precipitating agents in the Microfluidizer.

Figure 5-1. XRD pattern of $\text{La}_{0.2}\text{Sr}_{0.8}\text{FeO}_3$ synthesized by conventional solution precipitation technique and calcined at 590°C.

Figure 5-2. XRD pattern of the material synthesized by conventional solution precipitation technique showing evolution of the perovskite structure at a calcination temperature of 800°C .

Figure 5-3. XRD pattern showing evolution of perovskite structure in $\text{La}_{0.2}\text{Sr}_{0.8}\text{FeO}_3$ synthesized by the ethylene-glycol technique.

and the perovskite was precipitated from a mixture of the corresponding metal nitrates, while being subjected to cavitation forces. Water and 2-Propanol were used as solvents in both the conventional and the Microfluidizer synthesis techniques. The perovskites were characterized using XRD, DSC and TGA.

When the perovskite $\text{La}_{0.2}\text{Sr}_{0.8}\text{FeO}_3$ was synthesized in the Microfluidizer using NH_4OH as the precipitating agent and water as the solvent, the perovskite peaks appear at a calcination temperature of 590°C as shown in Figure 5-4. However, the peaks were split peaks, indicating that there was phase impurity. When the same synthesis procedure was employed but KOH was used as the precipitating agent in iso-propanol solvent, the perovskite formed was shown to be a pure phase material by its XRD pattern shown in Figure 5-5. The reason for this difference is attributed to the low value of solubility product of Strontium nitrate in the organic solvent, iso-propanol. In the synthesis procedure where water was used as the solvent, some of the strontium oxide was not precipitated, causing a lowered phase purity in the final material.

The use of an inorganic solvent such as iso-propanol and a strong base such as KOH as the precipitating agent made an efficient combination to produce materials of high phase purity even by the conventional (co-precipitation and stirring) synthesis technique. Figure 5-6 shows the XRD patterns obtained from SrLaFeO_3 using the conventional as well as the Microfluidizer technique using iso-propanol as the solvent for KOH . The phase purity of the conventional material was lower than that of the Microfluidizer synthesized material as evidenced by the shoulder of the perovskite reflection at 31.5° (2θ).

The difference in the materials formed by both these techniques was in the size of the particulates formed. While the conventional technique formed micron sized particulates, the Microfluidizer synthesis allowed the formation of nanometer sized particulates which were used in the pore-blockage experiments discussed in later sections.

Figure 5-4. Microfluidizer synthesized perovskite ($\text{Sr}_{0.8}\text{La}_{0.2}\text{FeO}_3$) using NH_4OH as the precipitating agent in water solvent.

Figure 5-5. Microfluidizer synthesized perovskite ($\text{Sr}_{0.8}\text{La}_{0.2}\text{FeO}_3$) using KOH as the precipitating agent in iso-propanol solvent.

Several other oxygen conducting perovskite materials were synthesized both by the Microfluidizer technique as well as the ethylene glycol technique. The relative amounts of strontium and lanthanum were varied for the above discussed perovskite, $\text{Sr}_x\text{La}_{(1-x)}\text{FeO}_3$. Other oxygen conducting perovskites such as $\text{SrCe}_{0.8}\text{Yb}_{0.2}\text{O}_3$ were also synthesized. Nanometer sized particulates of LaAlO_3 were synthesized in the Microfluidizer and were used to form the buffer layer for the pore filling experiments.

5.2.6 Characterization of perovskites by DSC

Differential Scanning Calorimetry (DSC) was used to characterize the perovskites prepared using the various techniques discussed above. DSC analysis gives information on the stability of the structure by recording the changes in heat content of the material. The data from DSC was correlated with the data from Thermo-Gravimetric Analysis (TGA) to differentiate between the enthalpies accompanying structural change and the heat loss associated with loss of volatiles (moisture, residual nitrates etc.). If the peaks registered in the DSC spectrum correspond to the heat of condensation of a volatile material, a weight loss would also be registered in the TGA spectrum at the corresponding temperature. Such peaks would appear only once during the heating cycle and this heat would not be recovered during the cooling cycle since the TGA and DSC measurements are carried out in a flowing stream of helium. On the other hand, the valleys (heat loss) that appear in the DSC spectrum during the heat cycle would appear as peaks (heat gain) during the cooling cycle only if the associated heat loss/gain is related to a structural change in the material. $\text{Sr}_{0.8}\text{La}_{0.2}\text{FeO}_3$ prepared both by the conventional and the cavitation techniques showed reversible exotherms on the DSC spectrum at 150°C and 350°C when KOH was used as the precipitating agent in 2-propanol medium. Using KOH in water resulted in the perovskite structure as evidenced by XRD, but this material did not show the reversible DSC exotherms. Since such reversible exotherms

Figure 5-6. XRD Spectra from samples of the $\text{Sr}_{0.8}\text{La}_{0.2}\text{FeO}_3$ prepared by the conventional and the cavitation techniques.

Figure 5-7. DSC spectra from a sample of $\text{Sr}_{0.8}\text{La}_{0.2}\text{FeO}_3$ showing the reversible exotherms and endotherms.

occur when a material undergoes structural or polymorphic changes, it is likely that the material prepared in 2-propanol resulted in perovskites with a defect structure in which there was a measurable energy difference between the two polymorphic forms as evidenced by the reversible exotherms at 150°C and 350°C as shown in Figure 5-7.

5.2.7 Comparison of catalytic activity of the perovskites

Methane coupling activity of the synthesized perovskite materials was tested by using these materials as catalysts in a quartz tube fixed bed reactor. Blank reactor experiments were performed in the non-porous quartz tube reactor at standard flow conditions typically used for the methane coupling experiments. Methane to oxygen ratio was maintained at 2.0, with a 10% oxygen dilution in helium. Methane conversions were found to be less than 5% over the temperature range 650°C to 850°C, indicating that the contribution from the quartz chips and the reactor tube walls was minimal.

Two perovskites, $\text{Sr}_{0.8}\text{La}_{0.2}\text{FeO}_3$ and $\text{SrCe}_{0.8}\text{Yb}_{0.2}\text{O}_3$ were tested for their catalytic activity towards methane coupling by packing the materials in a fixed bed non-porous reactor. The performance of both perovskites was compared with that of Sm_2O_3 over the temperature range of study. Figure 5-8 compares the methane conversions by all three materials, $\text{Sr}_{0.8}\text{La}_{0.2}\text{FeO}_3$, $\text{SrCe}_{0.8}\text{Yb}_{0.2}\text{O}_3$, and Sm_2O_3 operating under identical flow conditions. Catalyst loading of about 1 g was used for all these experiments. The catalyst was mixed with quartz chips and packed in the quartz tube, making up a 10 cm reaction zone. Over the entire temperature range of study, both the perovskite materials showed constant activity and stability over several hours on-line. Methane conversions were significantly higher than the blank reactor conversion of 5%. Over the entire temperature range studied, samarium oxide had 5-10% higher methane conversions than both the perovskites. $\text{SrCe}_{0.8}\text{Yb}_{0.2}\text{O}_3$ exhibited higher conversions than the $\text{Sr}_{0.8}\text{La}_{0.2}\text{FeO}_3$.

Figure 5-9 compares the C_2 selectivities of the three materials. Of the two perovskites, $Sr_{0.8}La_{0.2}FeO_3$ acts as a deep oxidation catalyst with very low C_2 selectivities, and no significant hydrocarbon yields. The C_2 selectivity of $SrCe_{0.8}Yb_{0.2}O_3$ lies midway between that of samarium oxide and $Sr_{0.8}La_{0.2}FeO_3$.

Although these studies were done using the perovskite materials in packed beds and not as membranes, the catalytic results suggest that the use of $Sr_{0.8}La_{0.2}FeO_3$ as a dense membrane material would be disadvantageous. We would like to synthesize dense membranes from materials that exhibit good oxygen conductivity at elevated temperatures, and at the same time, are good methane coupling catalysts, so that they would not lower the overall C_2 selectivity of the reactor. $SrCe_{0.8}Yb_{0.2}O_3$ is a more promising candidate since it has both methane coupling activity as well as oxygen conducting ability. Though literature reports do not indicate very high oxygen conductivity of this material, changes in relative compositions of cerium and yttrium are postulated to enhance the oxygen flux transported through the material. Hence, other compositions of this family of perovskites could serve as potential candidates for dense membrane synthesis.

5.3 Modification of porous gamma alumina membranes

One of our research objectives was to form a dense membrane by filling the 40 X pores of the γ -alumina alumina support with the oxygen conducting perovskite using the solution technique. However, γ -alumina alumina begins to undergo phase transformations at temperatures above 700°C to form β , δ , and finally α -alumina. This limits its use in high temperature applications. In this study, an γ -alumina membrane was modified by lanthanum oxide to stabilize the pore structure. The gamma alumina membrane tube used has a top-layer pore diameter of 40 X and thickness of about 1.5 μm .

Catalytic Testing for Oxidative Coupling of Methane
Quartz Tube Reactor, 12 cm Catalyst Bed

Figure 5-8. Comparison of CH_4 conversions during OCM for the two perovskites and samarium oxide.

Catalytic Testing for Oxidative Coupling of Methane
 Quartz Tube Reactor, 12 cm Catalyst Bed
 $\text{CH}_4 : \text{O}_2 : \text{He} :: 19.8 : 9.8 : 300 \text{ ml/min}$

- 1 gm $\text{Sr}_{0.8}\text{La}_{0.2}\text{FeO}_3$ Catalyst
- + 1 gm Sm_2O_3 Catalyst
- 1 gm $\text{SrCe}_{0.8}\text{Yb}_{0.2}\text{O}_3$ Catalyst

Figure 5-9. Comparison of C_2 selectivities for the OCM reaction from the two perovskites and Sm_2O_3 .

Before the modification, the gamma alumina membrane was cleaned by washing with DI water and drying at 120°C. The membrane tube was coated from the inside with a 50% $\text{La}(\text{NO}_3)_3$ aqueous solution for about 10 minutes. Then the tube was placed in a furnace and heated at a rate of 0.25 °C/min to 400°C and kept in the furnace overnight. These coating and calcination steps were repeated twice before the tube was finally calcined at 900°C.

Figure 5-10 shows the nitrogen permeance measurements on the gamma alumina membrane, before and after modification. The nitrogen permeance through the fresh gamma alumina membrane tube was 1.73×10^{-3} mol/Pa·m²·min. After the thermal treatment at 900°C for 7 hours, the nitrogen permeance of the gamma alumina membrane increased about 10 times. However, when the membrane was treated with $\text{La}(\text{NO}_3)_3$ solution and calcined at 900°C for 7 hours, the nitrogen permeance of the gamma alumina membrane was lower than that of the fresh gamma alumina membrane. An additional 50 hours' thermal treatment of the modified gamma alumina membrane only resulted in a slight increase in the nitrogen permeance.

Figure 5-11 shows the XRD patterns of the fresh γ -alumina membrane, the membrane after 900°C treatment, and the modified membrane after the 900°C thermal treatment. The γ -alumina phase in the top-layer of the fresh membrane could not be detected by XRD, and only the α -alumina phase of the transition layer was observed. This may be due to the fact that both the thickness and particle size of the top-layer were relatively small. The XRD patterns of the top-layer of the modified alumina membrane indicated that only the LaAlO_3 phase could be observed. This suggested that the formation of LaAlO_3 resulted in the improved thermal stability of the gamma alumina membrane, which is potentially important for high temperature porous catalytic membrane studies or as supports for thin dense membranes as shown in Section 5.4.1.

EDX digital mapping of the cross-section of the gamma alumina membrane tube showed that lanthanum was present across the entire thickness of the membrane tube wall, and more lanthanum was deposited in the top-layer than the support and transition layers.

5.4 Dense Membrane Synthesis by Filling up the Pores in a Porous Support.

5.4.1 Pore filling of modified porous γ -alumina membranes

An oxygen conducting perovskite ($\text{Sr}_{0.8}\text{La}_{0.2}\text{FeO}_3$) was deposited on the modified gamma alumina membrane by the solution deposition technique. The perovskite caused a lowering of permeance to gas flow at room temperature indicating that partial pore filling had occurred. XRD analysis of the deposit showed it to have the perovskite structure. Figure 5-12 shows the XRD pattern of the support, the powder perovskite and the porosity minimized support that was filled in with the perovskite.

The modification of the γ -alumina support membrane through the lanthanum nitrate treatment made the material thermally stable. Research efforts aimed at forming a dense membrane by filling the 40 Angstrom pores of the γ -alumina support by depositing the oxygen conducting perovskite $\text{Sr}_{0.8}\text{La}_{0.2}\text{FeO}_3$ from solution resulted in only partial success. While a decrease in gas permeation across the membrane was observed, complete pore blockage was not achieved. These results paralleled our earlier studies with solution depositions in α - alumina membranes discussed in Appendix A. In those experiments, both the conventional solution deposition, as well as the ethylene glycol sol-gel technique, were employed to synthesize the perovskites and deposit them inside

Figure 5-10. Permeance of Nitrogen through modified gamma alumina membrane.

Figure 5-11. XRD pattern of the modified gamma alumina membrane showing the formation of LaAlO_3 .

Figure 5-12. XRD spectra showing the alumina support structure, the $\text{Sr}_{0.8}\text{La}_{0.2}\text{FeO}_3$ perovskite (prepared by ethylene glycol sol-gel technique) powder pattern and the pore-filled support.

porous alpha alumina support membranes. Those efforts met with partial success in that though pore filling was accomplished and the gas permeation rate through the perovskite-deposited membranes decreased with increasing number of depositions, up to 7-8 depositions, dense membranes were not formed.

5.4.2 Pore filling of porous alpha alumina membranes.

Research work geared toward finding a robust way of making thin films of the perovskite materials led to efforts involving filling the pores in α -alumina membranes with nanometer sized particulates of perovskites. A thin film of oxygen-conducting material can be formed by the deposition of the precursor of the material derived by the sol-gel technique or by filling the pores with nanometer size grains of the material synthesized by the cavitation technique in the Microfluidizer. Cracks and pin-holes due to the differences in thermal expandability and surface properties between the material and the support are the major problems in the process of supported membrane preparation. These problems can be solved (or minimized) by choosing the same oxygen conducting material as support or by depositing a porous, transition (buffer) layer on the support on which the oxygen conducting dense membrane would be deposited. In the case of using the same material for this support, the porous support is prepared first by a hot-pressing or extruding technique with materials having larger particle size and then the dense layer can easily be formed using material with particles small enough to be densified during densification without changing the structure of the support. For depositing a buffer layer, a proper selection of the material should be made so as to match the lattices of both the support as well as the top layer that is to be deposited on the buffer layer.

In the work described below, an attempt was made to "lattice-match" the substrate with the perovskite material. Thermal stability of the pore-filled membranes that were prepared using the solution deposition and sol-gel techniques was limited and thermal cycling led to membrane failures. In the lattice-match approach described in the next section, it was attempted to first fill the large pores of the α - Al_2O_3 support with LaAlO_3

nano-particulates and then with $\text{Sr}_{0.8}\text{La}_{0.2}\text{FeO}_3$ nano-particulates. These nano-particulates were synthesized in the Microfluidizer.

The porous support material chosen for the pore-filling experiments was the 2000 Angstrom pore size $\alpha\text{-Al}_2\text{O}_3$ membrane discs obtained from Coors Inc. Experiments were tried where the oxygen conducting dense membrane perovskite material was deposited in the pores of this $\alpha\text{-Al}_2\text{O}_3$ support. These experiments were not successful in producing a crack free film since the high temperature calcination step (required in the perovskite synthesis procedure) always caused cracks and the perovskite would flake off. The relative inertness of the $\alpha\text{-Al}_2\text{O}_3$ support and the structural difference in the lattices of the support and the perovskite resulted in thermally induced defects in the pore-filled material.

By depositing a buffer layer of LaAlO_3 nano-particulates, also synthesized in the Microfluidizer to reduce the pore diameters, it was hoped that this combination of perovskite and nanostructured LaAlO_3 particles deposited in pores would result in a better lattice match with the perovskite $\text{Sr}_{0.8}\text{La}_{0.2}\text{FeO}_3$ than this perovskite and $\alpha\text{-Al}_2\text{O}_3$. This combination should provide a more robust structure since Al_2O_3 and LaAlO_3 are structurally and chemically similar, they have similar thermal coefficients of linear expansion.

The approach was taken to develop perovskite thin films by filling up the pores in large pore diameter support material such as $\alpha\text{-Al}_2\text{O}_3$ with nanometer sized perovskite particles synthesized in the Microfluidizer. By depositing a buffer layer of LaAlO_3 it was attempted to synthesize crack free films of oxygen conducting dense membranes on the porous $\alpha\text{-Al}_2\text{O}_3$ support.

Alpha alumina membranes with large pores (1.2 micron pore diameter) were used as the starting material. A high pressure technique based on *cavitation* effects in fluids

was used to synthesize nanometer size particles. The cavitation technique and the principle of operation of the Microfluidizer are discussed in detail in Appendix H. The solutions of lanthanum and aluminum nitrate were subjected to high pressure shear (20,000 psig) in the presence of ammonium hydroxide in the Microfluidizer to produce nanometer sized grains of LaAlO_3 with a particle agglomerate size of 0.5 microns. LaAlO_3 synthesized in the Microfluidizer was studied by XRD to determine phase purity of the material with increasing temperature of calcination as shown in Figure 5-13. A comparison with the JCPDS (Joint Committee on Powder Diffraction Studies) line spectra of LaAlO_3 showed that the perovskite structure formed after the 900°C calcination. On the basis of these results, the porous alpha alumina discs containing the LaAlO_3 gel produced in the Microfluidizer were calcined at 900°C .

Lanthanum aluminate nano-particles produced in the Microfluidizer were deposited inside the 1.2 micron pores of the alpha alumina substrate, partially filling the pores of the membrane. The pore-filling procedure involved forcing the nano-particulate suspension through the porous disc in a specialized pressure filter. The porous disc was used in place of a filter and the particulate suspension was forced through the porous disc under a pressure head of 60-70 psi. The particulates in the suspension deposit inside the pores of the support(filter) disc and form the filter cake right inside the pores of the support. The pore-filled disc is then calcined to 900°C to form LaAlO_3 in high phase purity. LaAlO_3 showed better adhesion to the alpha alumina support at high temperature, probably due to the fact that they have similar thermal expansion coefficient.

Figure 5-14 shows the change in gas permeance in the pore-filled alumina as a function of increasing number of pore fillings. The figure compares the gas permeance achieved in the pore filled alumina with that of 40 Å pore diameter gamma alumina and the 40 Å pore diameter Vycor.

The pore filled alumina was used as the support for depositing nano-particulates of $\text{Sr}_{0.8}\text{La}_{0.2}\text{FeO}_3$ synthesized in the Microfluidizer. Details on synthesis and characterization of the perovskite were discussed in the previous section. The perovskite nano-particulates were deposited on the LaAlO_3 overlay of the porous $\alpha\text{-Al}_2\text{O}_3$ support by filtering the nano-particulate suspension through the porous membrane under pressure until the filter cake formed in the pores of the support plugged up the pores and prevented further flow. The membrane was then calcined at 800°C to cement the deposit in the pores. By repeating this process 3 times, complete pore blockage was achieved. The dense membrane formed in the supported provided a gas tight seal at room temperatures. The dense membrane retained its integrity and was impervious to gas flow up to 400°C . Repeated thermal cycling beyond this temperature caused the membrane to break down and oxygen conduction through the membrane could not be tested, since oxygen transfer through the perovskite structure occurs only above 800°C .

The research involving pore-filling of a porous support to synthesize dense membranes led to a greater understanding of the material properties and membrane synthesis. Efforts to achieve a dense membrane resulted in only partial success. While technological improvements were achieved in the areas of support stabilization, progressive pore filling using nano-particulates that led to improved thermal stability, and dense membranes that were stable up to 400°C , the real breakthrough sought in synthesizing oxygen conducting dense membranes that could be used in the membrane reactor for studying the high temperature oxidative coupling of methane, were not achieved. Research efforts in the area of dense membrane reactors therefore concentrated on fabricating dense membrane pellet reactors and dense perovskite tubes that could be used in shell-and-tube reactors. These research efforts are discussed next.

Figure 5-13. XRD patterns of LaAlO_3 synthesized in the Microfluidizer showing evolution of crystallinity with increasing temperature of calcination.

Figure 5-14. Comparison of gas permeance in pore-filled alumina with increasing number of depositions of LaAlO_3 synthesized in the Microfluidizer.

5.5 Dense disk membrane preparation

Lanthanum-Iron-Cobalt-Strontium based perovskites, $\text{La}_{(1-x)}\text{Sr}_x\text{Fe}_y\text{Co}_{(1-y)}\text{O}_{3-\delta}$, have been prepared using the ethylene glycol synthesis technique and their perovskite structure has been confirmed by XRD analysis. These perovskites have been densified in the form of 0.5 inch diameter, 1/16 inch thick disks by the Cold-Uniaxial-Pressing at 1500 MPa followed by 1200°C treatment. Appendix B presents the details of the synthesis procedure.

These densified perovskite disks were fixed on the ends of nonporous tubes using a gold seal and oxygen permeation measurements were made at high temperatures. These cobalt based perovskites have been reported in the literature to have very high oxygen permeation rates, but our study has shown that these reported high oxygen permeation fluxes appear to be initial rate data. The steady state oxygen permeation through the $\text{La}_{0.2}\text{Sr}_{0.8}\text{Fe}_{0.2}\text{Co}_{0.8}\text{O}_{3-\delta}$ monitored over several hours is presented in Appendix B. Steady state oxygen flux was not obtained until after 50 hours. Prior studies in our laboratory showed that cobalt based perovskites are not very stable under reducing environments as compared to iron based materials. Hence perovskites with high iron content were studied and fabricated as tubes for dense membrane reactor studies.

5.6 Dense membrane reactor for oxidative coupling of methane

5.6.1 Dense membrane reactor set-up

A shell-and-tube reactor was used to study the oxidative coupling of methane in our laboratory. The dense membrane tubes were obtained from Argonne National Laboratory. As shown in Figure 5-15, The membrane tube served as the “tube”, and a quartz tube served as the “shell” side of the shell-and-tube reactor. Catalyst was packed on the inside of the dense membrane tube. Methane mixed with helium flowed in the tube side, while air was maintained at high pressure in the shell side. The two ends of the

Figure 5-15. Dense membrane reactor set-up

Figure 5-16. Oxygen permeance through the dense membrane tube

dense membrane tube were connected to quartz tubes. The reactor was heated to about 1000 °C in a helium atmosphere to make the seal between the membrane and the quartz tube. At temperatures above 750 °C, the dense membrane material allowed uni-directional transfer of oxygen, from the high pressure shell side, to the catalyst packed tube side. The use of a dense membrane, which was non-permeable to any species except oxygen, was intended to eliminate the loss of hydrocarbons from the reaction side to the oxygen-feed side.

5.6.2 Oxygen permeance through the dense membrane tube

The permeance of oxygen through the dense membrane tube was measured with air fed in the shell side of the reactor module and helium in the membrane tube. Figure 5-16 show the oxygen permeances at 950 °C and 910 °C. The oxygen permeance measurement at 950 °C was obtained without catalyst packing in the tube-side. The helium flow rate was kept at 45 cc/min except in the period from 2' to 8' in Figure 5-16, during which the helium flow rate was increased from 45 cc/min to 95, 180, and finally 245 cc/min. After that, the helium flow rate was reduced to the original value (45 cc/min). It can be seen from these results that the permeance reached a stable level within a relatively short period of time on stream compared to that reported by Balachandran et al. (1995). Also, the highest oxygen permeance observed was only 20 % of the reported value of 0.3 cc/min/cm² (Balachandran et al., 1995). This may have been caused by the relatively low flow rates of air in the shell side and the low flow rate of sweep gas in the tube side. The results at 910 °C in Figure 5-16 was obtained with catalyst packing. The oxygen permeance observed was consistent with the data at 950 °C. Again, the permeance was only about 20 % of the reported value of 0.3 cc/min/cm² by Balachandran et al. (1995). The oxygen permeance increases with an increase in either helium sweep flow rate or the air flowrate.

Figure 5-17 shows the oxygen permeance as a function of helium sweep flow rate in the tube side at 950°C and 1 atm. The oxygen permeance increases with increasing helium sweep flow rate.

5.6.3 Catalytic activity of the dense membrane material

In order to test the catalytic activity of the dense membrane $\text{SrFeCo}_{0.5}\text{O}_{3-x}$ under methane coupling condition, experiments were conducted in a dense membrane reactor with no catalyst packed in the tube side. Methane was fed to the tube side with helium and air had to the shell side of the reactor.

Table 5-1 shows the experimental results of the dense membrane reactor without catalyst at 950°C and 1 atm. The fact that the membrane material was a total oxidation catalyst was shown by the fact that carbon dioxide was the major product. However, a small amount of ethylene (rather than ethane) was observed in the product, probably due to the higher temperature, which favored the formation of ethylene rather than ethane. When reactions took place in the membrane tube, the partial pressure of oxygen was much lower (thus the oxygen partial pressure difference across the membrane was much higher) than that under non-reaction conditions. Therefore, the oxygen permeance shown in Table 5-1 was found to be about 4 times higher than that observed in the oxygen permeance measurement. This permeance was still less than the reported values during reaction (about 3 cc/min/cm²) and may have been resulted from the limited oxygen supply in the shell side, where 93 % of the oxygen was converted. This suggests that in future experiments, the oxygen flow rate across the membrane can be controlled by the flow rate as well as the oxygen partial pressure in the shell side.

Figure 5-17. Effect of helium sweep flowrate on the oxygen permeance of the dense membrane tube

Table 5-1 Experimental results of a blank run with a membrane reactor

Membrane tube geometry	L=9.3 cm, OD=6.5 mm, ID=4.5 mm
Temperature	950 °C
Pressure	1 atm
air flow rate (shell side)	10.5 cc/min
Methane flow rate (tube side)	3.8 cc/min
Helium flow rate (tube side)	45 cc/min
Methane conversion	31.8 %
Oxygen conversion (overall)	93.8 %
Oxygen conversion (tube side)	100 %
Carbon dioxide selectivity	80.2 %
Ethylene selectivity	19.8 %
Oxygen permeance	0.157 cc/min/cm ²

Figure 5-18 shows the methane conversion as a function of the initial feed ratio of methane to oxygen in the dense membrane reactor without catalyst at 850 °C and 1 atm. Again, no detectable C₂ hydrocarbons and oxygen were observed during these runs, and all the methane consumed was converted to carbon dioxide. Nearly 100% selectivity to carbon dioxide was observed as the result of the membrane material being a total oxidation catalyst.

After the experiment the membrane tube was examined by SEM (scanning electron microscopy). Figure 5-19 shows the entire cross section of the wall of membrane tube. With higher magnification, SEM images in the region close to the inner surface, middle of the wall, and the region close to the outer surface are shown in Figures 5-20a,

5-20b, and 5-20c respectively. It can be seen from these figures that the particle size gradually decreases from the outer surface, which was exposed to an oxidative atmosphere, to the inner surface, which was exposed to a reducing atmosphere. So, the particles of the membrane were broken down to smaller sizes under a reducing atmosphere.

5.6.4 Catalytic experiment in a packed-bed reactor with La/MgO catalyst

The oxygen-permeable dense membrane tube provided by Argonne National Laboratory was housed in a quartz tube as the shell of the membrane reactor. A quartz thermowell with 1 mm ID was inserted into the tube side and, in the annular space between the thermowell and the membrane tube, 1.5 g La/MgO catalyst was loosely packed to avoid breaking due to the thermal expansion of the catalyst during heating. It was reported that this catalyst showed a significant improvement in C_2 yield by using a distributed oxygen feed reactor over that of a conventional co-feed reactor [49].

Before running the catalytic membrane reactor, the oxygen permeance through the membrane was measured at reaction temperature. Also, a catalytic experiment with a conventional packed-bed reactor and a blank run in the membrane reactor without catalyst were conducted as a basis for comparison with the catalytic membrane reactor.

La/MgO catalyst has been prepared as the coupling catalyst. $Mg(OH)_2$ was first prepared by precipitation from aqueous $Mg(NO_3)_2$ solution by adding an excessive of 29% ammonia. Then the $Mg(OH)_2$ was dried at $180^\circ C$, crushed, and impregnated with $La(NO_3)_3$ solution. The mixture was dried at $110^\circ C$, followed by calcination at $550^\circ C$ overnight. Then the powder was pelletized, treated at $1000^\circ C$ for 10 hours, and sieved into 30-60 mesh. The X-ray diffraction pattern of the catalyst synthesized is shown in Figure 5-21. The major component was magnesium oxide (cubic) and lanthanum oxide. Although the mole ratio of La to Mg was 1:10, La was coated on the MgO support. The

Figure 5-18. Methane conversion at different methane to oxygen ratio of a dense membrane reactor without methane coupling catalyst

Figure 5-19. SEM picture of the entire cross-section of the membrane tube wall

Figure 5-20a. Cross-section view in the region close to the inner surface of the membrane tube

Figure 20b. Cross-section view of the central region of the membrane tube wall

Figure 20c. Cross-section view of the region close to the outer surface of the membrane tube

relatively smaller MgO peaks might be due to the fact that MgO was covered with La_2O_3 and the component La_2O_3 on the external surface contributed more to the XRD patterns than the support material MgO.

Figure 5-22 shows the methane conversion, C_2 selectivity, and C_2 yield at different initial methane to oxygen ratios with La/MgO as the catalyst in a co-feed packed bed reactor. These data were evaluated at a temperature of 790 °C, total pressure of 1 atm, oxygen flowrate of 1.6 cc/min and helium (as dilution gas) flowrate of 65 cc/min with 1.5 g La/MgO. As shown in Figure 5-22, as the methane to oxygen ratio increased from 1.8 to 11.4, the C_2 selectivity increased from 33.7% to 51.0%, while the methane conversion and C_2 yield dropped from 42.3% to 8.4% and from 14.2% to 4.3% respectively. The experimental results obtained are in agreement with those reported in the literature [49].

5.6.5 Experimental results with the catalytic dense membrane reactor

After the oxygen permeance measurement, methane was fed into the tube side and air into the shell side. No detectable C_2 hydrocarbons were observed in these experiments at temperatures of 770 to 910 °C. This suggested that the total oxidation of methane by the dense membrane material dominated the catalytic reaction in this configuration. Once CO_2 is formed, it cannot be reduced to C_2 hydrocarbons, in contrast to methane partial oxidation to syngas, where the CO_2 formation is the first step in producing CO and H_2 . In another experiment with the same reactor, instead of feeding air to the shell side as in the previous runs, air was co-fed with methane to the tube side and nothing was fed to the shell side of the membrane reactor. Since the methane coupling reaction took place in the catalyst bed before the reactant mixture contacted the total oxidation dense membrane material, 7% C_2 yield was observed during these runs. These results indicated that different contact modes of reactants with the catalyst resulted in different reactor performances.

5.6.6 Deposition of $\text{BaCe}_{0.6}\text{Sm}_{0.4}\text{O}_3$ on the dense membrane tube

As mentioned earlier, the dense membrane material is a total oxidation catalyst, and carbon dioxide was formed when the dense membrane interacted with the mixture of methane and oxygen. As a result, no C_2 hydrocarbons were observed in the product stream in a reaction carried out in a packed-bed dense membrane reactor. In order to prevent the deep oxidation of methane catalyzed by the direct contact of methane with the dense membrane material ($\text{SrFeCo}_{0.5}\text{O}_{3-x}$), the inner surface of the membrane tube was deposited with $\text{BaCe}_{0.6}\text{Sm}_{0.4}\text{O}_3$ by the sol-gel technique. Appropriate amounts of $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_3$, $\text{Ce}(\text{C}_2\text{H}_3\text{O}_2)_3 \cdot 1.5\text{H}_2\text{O}$, $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, and citric acid were dissolved in ethylene glycol and hydrochloric acid was added into the solution until all the salts were dissolved. Then the solution was heated for about 5 hours to form the gel. The inner wall of the dense membrane tube was coated with the gel and treated at 350°C overnight, followed by calcination at 1020°C for 5 hours. This procedure was repeated once more and the tube was installed into a membrane reactor set up for the catalytic experiments. The membrane tube before and after the deposition was studied by X-ray diffraction. Figure 5-23 shows the XRD patterns of the membrane tube before and after the sol-gel deposition of $\text{BaCe}_{0.6}\text{Sm}_{0.4}\text{O}_3$. The XRD pattern at 1180°C shows no reflection for $\text{BaCe}_{0.6}\text{Sm}_{0.4}\text{O}_3$ and only peaks for the membrane material indicating that it was applied as a very thin layer.

5.6.7 Catalytic study of the dense membrane reactor after the coating of $\text{BaCe}_{0.6}\text{Sm}_{0.4}\text{O}_3$

After the deposition, the tube was installed into a membrane reactor set up with the La/MgO catalyst packed inside the membrane tube. Figure 5-24 shows the C_2 selectivity vs methane conversion at 810°C and 1 atm. Figure 5-24 shows that the

Figure 5-21. XRD pattern of the La/MgO catalyst

Figure 5-22. Methane coupling in a co-feed packed-bed reactor with La/MgO catalyst

Figure 5-23. The XRD patterns of the dense membrane tube before and after the sol-gel deposition of BaCe_{0.6}Sm_{0.4}O₃

Figure 5-24. C₂ selectivity vs methane conversion plots of the dense membrane reactor and co-feed packed-bed reactor

membrane reactor gives higher C_2 selectivity than the co-feed reactor for the same methane conversion level. However, the C_2 yield is still less than 10%. This may have resulted from the non-complete coverage of the inner wall of the membrane tube by the deposited $BaCe_{0.6}Sm_{0.4}O_3$ material.

5.6.8 Improvement of the $BaCe_{0.6}Sm_{0.4}O_3$ -coating procedure

To improve the quality of the coating film, the inner surface of the fresh dense membrane tube was pre-treated followed by the twice deposition of $BaCe_{0.6}Sm_{0.4}O_3$ material by the sol-gel technique. Hydrochloric acid was the first pretreatment solution used. Figure 5-25 shows the percentage weight loss of the dense membrane tube ($SrFeCo_{0.5}O_{3-x}$) as a function of time when the membrane was pretreated with 1 N hydrochloric acid. After having been in the solution for 2 minutes, the membrane tube was taken out from the solution, washed, dried at 120°C for 10 minutes, weighed, and put into 10 ml fresh hydrochloric acid solution in 5-minute intervals. Due to the reaction between the metal oxides and the hydrochloric acid, the membrane tube quickly lost about 22% of its original weight in 27 minutes. Another solution used was a basic solution prepared by dissolving 44 g Na_3PO_4 , 65 g Na_2CO_3 , and 45 g NaOH in 1000 ml DI water. The treatment was conducted in a Erlenmeyer flask placed in an ultrasonic bath for 30 minutes. The weight loss after the treatment was less than 0.2%.

In the coating step, the inner surface of the dense membrane tube was coated with $BaCe_{0.6}Sm_{0.4}O_3$ by the sol-gel technique. First, the membrane was dip-coated with the sol prepared by the procedure reported earlier. The membrane was treated at a heating rate of

Figure 5-25. Weight loss of the dense membrane tube in 1 N hydrochloric acid at 22°C

Figure 5-26. Scanning electron micrograph of the original membrane surface.

Figure 5-27a. Scanning electron micrograph of the membrane surface without surface treatment

Figure 5-27b. Scanning electron micrograph of the membrane surface with hydrochloric treatment

Figure 5-27c. Scanning electron micrograph of the membrane surface with basic solution treatment

1°C/min to 250°C and was kept at 250°C for 6 hours. Then, the temperature of the furnace was raised, at a rate of 1.5°C/min, to 1000°C, where it was kept at 1000°C for 5 hours for calcination. The membrane was finally cooled down to room temperature at a cooling rate of 1.5°C/min.

For comparison, the original membrane surface is shown in Figure 5-26. Figure 5-27 shows the SEM pictures of the membrane surfaces after the membrane was coated with $\text{BaCe}_{0.6}\text{Sm}_{0.4}\text{O}_3$ by sol-gel technique. Figures 5-27a, 5-27b, and 5-27c are the membrane surfaces without surface pretreatment, with hydrochloric acid treatment, and with basic solution treatment, respectively. If the surface was not pretreated, it was difficult to cover the membrane surface evenly with the coating material ($\text{BaCe}_{0.6}\text{Sm}_{0.4}\text{O}_3$). With hydrochloric acid, although the coated material was more evenly distributed, the surface became rough, which probably resulted from the unequal reaction rates of the three metal oxides with hydrochloric acid. In the case of the basic solution pretreatment, the membrane surface was well covered with the coating material.

5.7 Catalytic $\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_3$ perovskite membrane reactor for the oxidative coupling of methane

The catalytic oxidative coupling of methane [14, 31, 38, 41] is one of the most extensively studied subjects in catalysis in an effort to utilize the abundant resources of natural gas. A wide variety of catalysts [150] have been identified since the pioneering work of Keller and Bhasin [36]. However, they all suffer from relatively low C_2 hydrocarbon selectivity at higher methane conversions due to the complete oxidation of methane and C_2 products. The key challenge facing the commercialization of methane oxidative coupling is to suppress the complete oxidation of methane and the desired products (C_2 hydrocarbons).

One of the proposed strategies to achieve high C_2 selectivity at higher methane conversion is to use porous or dense ceramic membrane reactors instead of the conventional packed-bed reactors. With a membrane reactor, the oxygen can be supplied to the reactor in a controlled way and higher C_2 selectivity can be achieved due to the relatively lower oxygen partial pressure in the reaction side. Compared to porous membrane reactors [50, 51a, 51b, 116, 122, 151], dense membrane reactors offer the possibility of supplying the oxygen in a form that circumvents the gas phase and forms active oxygen species. Because the oxygen first reaches the catalyst through the membrane and forms active surface-oxygen species, the undesired gas-phase reactions of oxygen with methane or its intermediates could be greatly reduced. In addition, the dense membrane reactors allow selective passage of oxygen gas to the reaction zone and cheaper oxygen sources (such as air) can be used without need of downstream nitrogen separation from the product stream.

Eng and Stoukides [152] reviewed the early work using dense membranes for methane coupling. The first solid-oxide membrane reactor for methane coupling was reported by Otsuka et al. [153], who used a YSZ (yttrium-stabilized zirconia) membrane as an oxygen pump. Guo et al. [154] investigated the effects of oxygen flux, temperature and feed concentration on the performance of oxidative coupling of methane using a 1 wt % $Sr/La_2O_3-Bi_2O_3-Ag$ -YSZ solid oxide membrane reactor, and C_2 yields up to 8% were achieved at a C_2 selectivity of 75%. A ceramic membrane proposed by Hazbun [54] was reported to be comprised of an impervious outer layer of mixed conducting zirconia and a porous inner layer of magnesia-stabilized zirconia with the catalyst inside. Yttrium-stabilized zirconia is a well-known oxygen ion conductor. However, its application as a membrane material for the oxidation reactions has been limited by a low oxygen flux, due to the low electronic conductivity.

Mixed electron/anion conductors with perovskite structures such as $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-z}$ exhibit both high electronic and ionic conductivities [155, 156, 157]. Partial substitution of Sr for La and Fe for Co could increase the ionic-electronic conductivity [155, 156] as well as the catalytic activity for OCM [158]. However, the presence of La is necessary for the stability of this type of material [159]. Balachandran et al. [160] found that the dense membrane material $\text{La}_{0.2}\text{Sr}_{0.8}\text{Fe}_{0.2}\text{Co}_{0.8}\text{O}_x$ was unstable under the conditions of methane partial oxidation reactions due to a phase transformation. Although a non-perovskite material, such as $\text{SrCo}_{0.5}\text{FeO}_3$, showed much better structural stability [161], it had no activity towards OCM reaction [146]. Another non-perovskite, $\text{LaCo}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$, was also found to have no activity for OCM [162].

Xu and Thomson [163] investigated OCM in a La-Ba-Co-Fe-O perovskite membrane reactor. Although they did not report methane conversion, higher C_2 selectivities (up to 50%) were achieved in the membrane reactor than in the cofeed reactor. Using a proton-hole mixed conductor ($\text{Sr}_{0.95}\text{Yb}_{0.05}\text{CeO}_{3-\delta}$) as a membrane reactor, Iwahara and his co-workers [164] carried out methane coupling reactions. The permeation and removal of hydrogen enhanced the formation of C_2 hydrocarbons, by reacting with oxygen, on the side opposite to the methane-feeding side of the membrane. Although there were no carbon oxides formed, the conversion was less than 1%, probably due to low hydrogen fluxes and/or the low activity of the catalyst they used. Elshof et al. [165] used an ionic-electronic mixed-conducting perovskite-type oxide $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ as a dense membrane for oxygen supply in a reactor for methane coupling. C_2 selectivities up to 70% were achieved. Still, the methane conversion was low (only 1-3%). Hibono et al. [166] studied the OCM using a disk-type membrane reactor with $\text{BaCe}_{1-x}\text{Gd}_x\text{O}_{3-\delta}$ prepared by a solid state reaction method. The experiments were conducted at low methane conversion levels (below 20%) and higher C_2 selectivity was observed in the membrane reactor than in the co-feed reactor.

In summary, although C_2 selectivity of up to 95% has been reported for the oxidative coupling of methane, the yields obtained with the dense membrane reactors are generally low (between 1% and 10%). Almost all of the OCM dense membrane reactor studies reported in the literature were carried out on membrane disks (rather than on tubes). These types of reactors are essentially well-mixed flow reactors (CSTR). According to the modeling results obtained by Guo et al. [154], higher C_2 selectivity and methane conversion can be achieved under plug flow conditions compared with well-mixed flow conditions. This suggests the advantage of using a tube-type (rather than disk-type) dense membrane reactor for OCM.

A dense membrane tube made from $BaCe_{0.8}Gd_{0.2}O_{3+x}$ by the ethylene glycol method, was used for the oxidative coupling of methane. C_2 yields of up to 16% were observed in the dense membrane reactor.

5.7.1 Experimental

5.7.1.1 Synthesis and fabrication of the BCG dense membrane tube

The $BaCe_{0.8}Gd_{0.2}O_3$ powder was prepared by the ethylene glycol method. Stoichiometric amounts of the corresponding metal acetates were dissolved in a solution of ethylene glycol and nitric acid. $Ba(CH_3CO_2)_2$ (99%) was purchased from Aldrich, and $Ce(CH_3CO_2)_3 \cdot 1.5H_2O$ (99.9%) and $Gd(CH_3CO_2)_3 \cdot 4H_2O$ (99.9%) from Alfa. For 1 mole of BCG powder, about 480 ml of nitric acid (70%) was used, and the ethylene glycol was added until the total volume of the solution was about 7.75 liter. The homogeneous solution was agitated overnight and transferred into a beaker covered by a watch glass.

Then the solution was stirred by a magnetic stirring bar and evaporated on a hot plate at about 200°C for about 24 hr, followed by a spontaneous combustion. The fine powder was crushed and calcined at 1000°C for 10 hours in air. Figure 5-28 shows the X-ray diffraction patterns of the material at room temperature after calcination at 800°C, 1000°C, and 1200°C. The 800°C pattern shows that the synthesis resulted in a mixed phase. Calcination to higher temperatures (Fig. 5-28(b) and 5-28(c)) shows the presence of an essentially pure perovskite phase. The reflection near 67.22 degrees indicates a slight tetragonal distortion in the 1000°C sample which is converted to the pure cubic phase at 1200°C. The high phase purity offered by the synthesis technique is especially favorable for densification into an oxygen-conducting membrane.

To prepare for extrusion, the calcined ceramic powder was mixed with several additives to make a formulation (slip) with enough plasticity to be easily formed into tubes while retaining satisfactory strength in the green state. The additives included a solvent (butanol or xylene), a dispersant, a binder, and a plasticizer. After the slip was prepared, some of the solvent was allowed to evaporate, which yielded a plastic mass that was forced through a die at 20 MPa to produce a hollow tube. The extruded tube had an outside diameter of 6 mm and an inner diameter of 4.6 mm, and length up to 30 cm. The extruded tube was heated at 5°C/h in the temperature range of 150-400°C to facilitate the removal of the gaseous species formed during decomposition of the organic additives. After that the heating rate was increased to 60°C/h and the tube was sintered at 1350°C in stagnant air for 5-10 h.

5.7.1.2 Membrane reactor experimental setup

A shell-and-tube reactor was used in this study. The membrane reactor configuration is shown in Figure 5-15. The membrane tube served as the tube, and a

Figure 5-28. X-ray diffraction patterns of the membrane material: (a) calcined at 800°C; (b) calcined at 1000°C; (c) calcined at 1200°C

quartz tube served as the shell side of the shell-and-tube reactor. No catalyst was packed inside of the dense membrane tube. A quartz thermowell (1 mm i.d. and 3 mm o.d.) was positioned along the axis of the membrane tube and allowed a sliding thermocouple to profile the temperature along the reactor. A cylindrical heater with a PID controller maintained the temperature of the reactor. The heated zone (between the shell side inlet and outlet on the quartz jacket) was about 40 cm long. The membrane tube (length = 11 cm long, I.D. = 4.6 mm, and O.D. = 6 mm) was connected with a quartz tube (quartz plunger in Figure 5-15) with Vycor glass O-rings on both ends of the membrane tube. The seal was made by heating the reactor slowly to about 1000°C in a stagnant atmosphere.

Methane mixed with helium was fed from the tube side, while air (or the mixture of oxygen and helium) was fed to the shell side. In the case of co-feed reactor operation, the mixture of methane, oxygen, and helium was fed to the tube side. The product stream withdrawn from the bottom of the tube side was mixed with a constant flow of argon (which served as an internal standard) and analyzed by an on-line gas chromatograph (HP5890 Series II) with a mass spectrometer detector (HP 5971). Mass flow controllers (Brooks 5850C), which were calibrated by a digital bubble flow meter (Alltech Co.), regulated the flow rates of all the gases which flowed into the reactor, and the argon.

A Poraplot-Q megabore column (0.53 mm i.d., purchased from Alltech Co.) was used to resolve methane, ethylene, ethane, and carbon dioxide peaks, while argon, carbon monoxide, and oxygen peaks that co-eluted were resolved by the mass spectrometer. Concentrations of CH_4 , O_2 , C_2H_4 , C_2H_6 , CO and CO_2 were computed by calibrating against a standard gas mixture containing all of the product species in known quantities.

5.7.2 Results and discussion

5.7.2.1 Temperature dependence of the oxygen permeation rate through the membrane tube

The oxygen permeation rate was measured by feeding air in the shell side and helium in the tube side. Figure 5-29 shows the oxygen fluxes at helium flow rates of 26 cc/min and 108 cc/min as functions of temperature. The air flow rate was kept at 78.3 cc/min during these measurements. Over a temperature range of about 300°C, the oxygen flux increased by a factor of 5.

An increase in the helium sweep flow rate in the tube side reduces the oxygen partial pressure in the tube side, thus resulting in a higher oxygen partial pressure difference across the membrane. The oxygen flux is, therefore, observed to increase with helium sweep flow rate. The semi-logarithm plot of oxygen flux versus the reciprocal of absolute temperature ($1/T$) fell closely on a straight line. Based on the Arrhenius plot, the activation energies for oxygen permeation for the helium sweep rates of 26 cc/min and 108 cc/min were 57.9 and 58.7 kJ/mol, respectively. These two values of activation energy were essentially the same, within the error limits.

The oxygen flux at 900°C at an oxygen partial pressure of 1 atm and a helium sweep flow rate of 26 cc/min was about 0.055 cc/cm²/min. This is about 55% of the value reported by Hibino et al. [166] for a disk (diameter = 12 mm; thickness = 0.35 mm) made from the same membrane material. However, considering the fact that the wall of the membrane tube used in this study was twice as thick as the disk [166], the oxygen permeabilities should be much closer to each other than the fluxes. The oxygen flux is similar to what we observed in previous work with the SrCo_{0.5}FeO_x membrane tube [146].

Figure 5-29. Arrhenius plot for the oxygen flux through the $\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_{3-x}$ (BCG) membrane, at 778°C. Oxygen/helium (shell) flow = 80 cc/min and helium (tube) = 26 cc/min

5.7.2.2 Effect of oxygen partial pressure on the oxygen flux through the membrane tube

The oxygen fluxes through the $\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_3$ (BCG) dense membrane tube were measured at different shell-side oxygen partial pressures. A mixture of oxygen and helium was fed to the shell side of the membrane tube. The partial pressure of oxygen in the shell side was changed by varying the flow rates of oxygen and helium. The total flow rate in the shell side was kept at about 80 cc/min and the shell side outlet was open to the atmosphere. Helium (26 cc/min) was fed from the top of the reactor into the tube side. The mixture of oxygen and helium was withdrawn from the bottom of the membrane tube side and analyzed by on-line gas chromatography.

According to Wagner's equation [167], the oxygen flux should be proportional to $\ln(P_{\text{O}_{2,s}}/P_{\text{O}_{2,t}})$, where $P_{\text{O}_{2,s}}$ and $P_{\text{O}_{2,t}}$ are the oxygen partial pressure in the shell and tube side, respectively. Figure 5-30 shows the oxygen flux as a function of the ratio of the constant oxygen partial pressure in the shell side to that at the exit of the tube side at 778 °C. The partial pressure of oxygen was calculated based on the measured flow rates of oxygen and helium in the shell side and the tube side. On the semi-logarithm plot, the oxygen flux increases linearly with the oxygen partial pressure ratio. This confirms that Wagner's equation describes permeation through the present membrane, and suggests that the controlling resistance was diffusion through the BCG tube wall, rather than surface resistances. In addition, the straight-line fit of the data extrapolates almost exactly to zero flux when the ratio of the partial pressures is unity, as expected.

Figure 5-30. Oxygen fluxes as a function of oxygen partial pressure ratio across the membrane, at 778°C. Oxygen/helium (shell) flow = 80 cc/min and helium (tube) = 26 cc/min.

5.7.2.3 Methane oxidative coupling using the BCG membrane reactor

Methane oxidative coupling reactions were carried out in the BCG dense membrane reactor with no catalyst packed in the tube side. A mixture of air and helium was fed from the shell side while the mixture of methane and helium was fed from the top of the reactor into the tube side. For comparison purposes, the reactor module was also run in a co-feed mode by feeding the mixture of methane, oxygen, and helium into the tube side.

Figure 5-31 shows the C_2 selectivity - methane conversion plots for both membrane and co-feed reactors at 778°C. The methane flow rate was kept at 1.4 cc/min. For the membrane reactor, the methane conversion was changed by changing the oxygen to helium ratio in the shell side, while for the co-feed reactor, the methane conversion was changed by varying the oxygen flow rate in the tube side. When the reactor was operated in the co-feed mode, C_2 yields up to 13% were obtained, which indicated that the BCG membrane was a fairly good OCM catalyst. For both membrane and co-feed reactor, the C_2 selectivity dropped rapidly as the methane conversion increased. The highest C_2 yield was about 16.5% (observed at a selectivity of 62.5%). Although the membrane reactor showed slightly higher selectivity than the co-feed reactor at the same methane conversion level, the steep drop in C_2 selectivity as a result of the increase of oxygen partial pressure in the shell side indicated that the non-selective, gas phase reactions still played a significant role.

Figure 5-32 shows the BCG dense membrane reactor performance at different shell-side oxygen partial pressures. As the oxygen partial pressure in the shell side

Figure 5-31. C₂ selectivity – methane conversion plots for the membrane and co-feed reactors, at 778°C. Methane flow rate = 1.4 cc/min.

Figure 5-32. Effect of oxygen partial pressure in the shell side on membrane reactor performance, at 778°C. Methane flow rate = 1.4 cc/min.

increased, a decrease in C_2 selectivity and an increase in the methane conversion were observed. The C_2 yield remained approximately constant over the entire oxygen partial pressure range used in the experiments. As suggested by Xu and Thomson [163], the oxygen transport rate through the membrane is higher than the OCM reaction rate on the surface. This allows molecular oxygen to be formed via the recombination of oxygen ions. This gas phase oxygen can then contribute to the complete oxidation of the C_2 products. To improve the OCM performance of the membrane reactor, a more active material should be used as the membrane material or should be deposited on the reaction side surface of the membrane tube.

The OCM experiments were conducted using the dense membrane tube for over one month without any detectable helium leak or mechanical failure and the oxygen flux remained unchanged. This indicates that the membrane tube was mechanically and chemically stable under the OCM reaction conditions.

5.7.3 Summary

Oxidative coupling of methane was studied with a shell-and-tube type dense membrane reactor. The membrane tube was made by extrusion with $BaCe_{0.8}Gd_{0.2}O_3$ prepared by the ethylene glycol method. C_2 hydrocarbon yields up to 16% were achieved in the membrane reactor. Although the improvement in C_2 hydrocarbon yield was not significant versus co-feeding oxygen and methane in the same dense membrane reactor setup, the use of the oxygen-permeable dense membrane reactor offers the advantage of using air as the oxygen source without downstream separation of nitrogen. The dense membrane remained stable after continuous running for one month.

Chapter 6. Porous Alumina Membrane Reactor

Although the use of dense membrane reactors in OCM eliminated the methane loss through the pores encountered in the porous membrane reactors, the selectivities and yields toward the C_2 hydrocarbons in the dense membrane reactors were still not high enough due to the total oxidation catalytic activity of the dense membrane materials themselves. The stabilization of the gamma alumina membrane allows us to utilize its fine pore structures at high temperatures and to maintain reasonable pressure drop across the membrane so that the delivery of oxygen can be controlled for OCM. By keeping a sufficient pressure drop across the membrane and blocking the shell side outlet of the membrane reactor, the loss of both methane and C_2 hydrocarbon products could be substantially reduced. Since alumina has much less total oxidation catalytic activity than the perovskite materials, the stabilized gamma alumina membrane offers the potential to achieve higher C_2 selectivities and yields.

Porous gamma-alumina membrane tubes were stabilized by treating the membrane tube with $La(NO_3)_3$ and calcining at $900^\circ C$ to form $LaAlO_3$. Using a Mn-W-Na/SiO₂ catalyst, methane oxidative coupling experiments were conducted in the modified porous gamma alumina membrane reactor for the first time, and its performance was compared with a packed reactor operated at similar conditions. C_2 yields up to 27.5%, which is the highest for membrane reactors ever reported in the literature, were obtained in the membrane reactor. The experimental results clearly demonstrated the beneficial effect of the distributed feed of oxygen along the reactor length for the methane oxidative coupling reactions.

6.1 Porous Alumina Membrane Research Objective

The objective of conducting the OCM reactions using the porous alumina membrane reactor was to develop a porous membrane reactor that could be used at high

temperatures for OCM with high C_2 selectivity and yield. By stabilizing the gamma alumina membrane, the gamma alumina membrane could be used at high temperatures without increasing the pore size, as would happen to the un-stabilized gamma alumina as a result of high temperature phase transformation. At the same time, the pressure drop across the stabilized gamma alumina membrane would reduce the losses of methane or the hydrocarbons from the catalyst-bed side of the membrane reactor.

6.2 Modification of porous gamma alumina membranes

The commercially available porous ceramic membrane tubes such as alumina and zirconia membranes are radially asymmetric. Typically, the thickness of the top-layer ranges from $2\mu\text{m}$ to $10\mu\text{m}$. The top-layer is built up by gamma alumina deposition onto two or three intermediate layers and a support structure which are all made up of increasingly larger grains of alumina. Due to the small thickness of the top layer and relatively large pore diameters (e.g. 500 Angstrom and higher) of alpha alumina and zirconia membranes in the top layer, relatively high gas fluxes are obtained for small values of pressure drop across the membranes. Therefore, alpha alumina membranes could not be used directly for metering oxygen flow in porous membrane reactors.

Gamma alumina membranes are available with a pore size of 40 Angstroms and the pressure drop across the membrane is higher than for alpha and zirconia membrane tubes. Compared to the porous Vycor glass membrane tube, the gamma alumina membrane has better mechanical strength. As described in Chapter 5 (Section 5.4.1), the thermal stability of the gamma alumina membrane can be improved by modifying the gamma alumina membrane with $\text{La}(\text{NO}_3)_3$ followed by heat treatment at 900°C .

The gamma alumina membrane tube was purchased from US Filter. Figure 6-1 is the SEM picture of the gamma alumina membrane tube in the region close to the top-layer. The top-layer of the membrane had a pore diameter of 40 Angstrom and a thickness of about $3\mu\text{m}$.

Figure 6-1. Cross-section view of the gamma alumina membrane tube

The modification of the gamma alumina membrane with lanthanum nitrate makes it possible to use the gamma alumina membrane tube for higher temperature applications such as OCM to achieve significant pressure drop across the membrane. This technique is easier to apply than the coating methods (i.e. sputtering coating, CVD deposition, etc.). Since the top layer is the same material as the support layer, the formation of cracks due to the difference in thermal expansion is minimized.

6.3 Membrane reactor setup

After the modification the gamma alumina membrane tube (14.2 cm long) was welded to a 19 cm long non-porous alumina tube on each end of the membrane tube with a high temperature glaze [122]. The curing process of the glaze was started at room temperature overnight, followed by treating at 60, 90, and 120°C for 2-3 hours at each stage.

The lanthanum stabilized gamma alumina membrane tube was installed into the membrane reactor setup. A shell-and-tube reactor was used to study the oxidative coupling of methane. Figure 6-2 shows the membrane reactor module. The membrane tube served as the "tube, and a stainless steel tube with quartz -lining served as the shell side of the shell-and-tube reactor. Mn-W-Na/SiO₂ catalyst was packed in the annular space between the gamma-alumina membrane (I.D.=7 mm) and the thermowell (I.D.=3 mm) placed concentrically inside the reactor tube. The height of the packed-bed was about 14 cm. Methane was fed to the tube side and a mixture of oxygen and helium was fed to the shell side at pressures slightly above atmospheric pressure for both the tube and shell sides. Although the porous gamma alumina membrane was successfully modified by lanthanum nitrate, some of the methane and C₂ hydrocarbons produced could still diffuse through the membrane and get completely oxidized in the shell side of the reactor. In order to reduce the amount of hydrocarbon loss from the tube to the shell side, the outlet of the shell side was blocked. For comparison purposes, the membrane reactor was also operated in the co-feed mode by feeding the mixture of methane and oxygen to the tube side and helium to the shell side with the shell side outlet blocked. The composition of the product was analyzed with a gas chromatograph equipped with a mass spectrometer analyzer.

The Mn-W -Na\SiO₂ catalyst was prepared by incipient wetness impregnation, at 80-85°C, onto a silica gel support (Davison, grade 643) with aqueous solutions with appropriate concentrations of Mn(NO₃)₃ (Aldrich, 98%) and Na₂WO₄ (Alfa, 98%) such that the final composition of the catalyst was Mn:1.9 wt% and Na₂WO₄: 5 wt% . Then the catalyst was dried at 130°C for 8 h, calcined at 850°C for 8 h, pelletized, calcined at 1000°C for 4 hours, crushed and sieved to 35-60 mesh size [123].

Figure 6-2. Porous alumina membrane reactor module

6.4 Catalytic experimental results.

Methane oxidative coupling experiments were conducted in a porous gamma alumina membrane reactor using Mn-W-Na/SiO₂ catalyst, and its performance was compared with a packed reactor operated at similar conditions. The gamma-alumina membrane tube was stabilized by treating the membrane tube with a La(NO₃)₃ aqueous solution and calcining at 900°C. The experimental results reported below clearly demonstrated the beneficial effect of distributed feed of oxygen along the reactor length for the methane oxidative coupling reactions.

Although the membrane reactor showed lower methane conversion at the same reaction conditions, it gave higher C₂ selectivity and C₂ yield at similar methane conversions. By varying the helium flow rate and keeping the temperature, methane flow rate, and oxygen flow rate constant, the membrane reactor gave 10% higher C₂ yield and 30% higher C₂ selectivity than the co-feed reactor operated at the same methane conversion. At similar C₂ yield and C₂ selectivity, the methane conversion of the membrane reactor was 15% lower than that of a co-feed reactor. By varying the oxygen flow rate and keeping the temperature, methane flow rate, and helium flow rate constant, at the same methane conversion, the membrane reactor gave about 3% higher C₂ yield and C₂ selectivity than the co-feed reactor. Higher helium flow rate gave higher C₂ selectivity and yield, whereas changing methane flow rate did not significantly affect the reactor performance.

6.4.1 Effect of dilution gas

Figure 6-3 and Figure 6-4 show the C₂ selectivities and yields as functions of methane conversion of the membrane and co-feed reactors at 805°C and methane and oxygen flow rates of 6.5 cc/min and 3.7 cc/min respectively. For both the membrane and co-feed reactors, the helium flow rates were varied over a range of 0-212 cc/min, while the temperature, methane flow rate, and oxygen flow rate were kept the same.

Figure 6-3. Comparison of C₂ selectivities in a membrane and co-feed reactor as functions of methane conversion

It can be seen that the membrane reactor gave lower methane conversions than the co-feed reactor. This is due to the difference in the feeding mode between the two types of reactors. The separated feed of methane and oxygen from the tube and shell sides in the membrane reactor resulted in the lower average partial pressure of oxygen in the tube side (and thus the lower average reaction rate and lower methane conversion).

If the two reactors are compared at similar methane conversions (i.e. 46%), the membrane reactor has 30% higher C₂ selectivity and 10% higher yield than the co-feed reactor. If the two reactors are compared at the same C₂ selectivity and C₂ yield, the methane conversion of the membrane reactor is 15% lower than that of the co-feed reactor. This means that, for the same amount of C₂ hydrocarbons produced, less methane was consumed by using a membrane reactor.

Figure 6-4. Comparison of C₂ yields in a membrane and co-feed reactor as functions of methane conversion

If the two types of reactors are compared in the C₂ selectivity-C₂ yield plot as shown in Figure 6-5, the membrane reactor gives about 10-15% higher selectivities than those of the co-feed reactor. These experimental data clearly demonstrated the beneficial effect of distributed feed of oxygen along the reactor length for the methane oxidative coupling reactions.

Both plots of C₂ selectivity versus methane conversion and C₂ yield versus methane conversion in Figure 6-3 and Figure 6-4 have positive slope, which is contrary to

Figure 6-5. Comparison of C₂ selectivities in a membrane and co-feed reactor as functions of C₂ yield

the general results reported in the literature, where the C₂ selectivity - conversion plot always has a negative slope (or, higher conversion corresponds to lower selectivity). As mentioned above, the helium flow rate is the only variable in these plots. Increasing helium flow rate reduced the residence time, which in turn reduced the extent of C₂ oxidation and increased C₂ selectivity. Since the oxygen conversions are close to 100% in these runs and less oxygen is consumed to produce C₂ hydrocarbons than CO_x (CO and CO₂), the higher helium flow rates resulted in higher methane conversions and C₂ selectivity in both reactor configurations.

At higher helium flow rate, the residence time of methane was short and the partial pressure of the reactants (methane and oxygen) became low, thus, some of the

oxygen was left over unreacted at the outlet of the membrane reactor. As a result, the C_2 yield of the membrane reactor began to drop after the helium flow rate exceeded a certain value. For the co-feed reactor, where the average oxygen partial pressure was higher, it could be operated under higher helium flow rates without dropping the methane conversion. Therefore, it can be predicted that higher C_2 yield would be realized in the membrane reactor if a longer reactor (or larger catalyst volume) were used.

Figure 6-6. Comparison of C_2 selectivities in a membrane and co-feed reactor as functions of helium flow rate.

The reactor performance as a function of helium flow rate is shown in Figure 6-6. Higher C_2 selectivity was observed in a membrane reactor at helium flow rates higher than 40 cc/min. It can be seen from Figure 6-6 that higher C_2 selectivity in a membrane

reactor mainly resulted from the higher ethane selectivity and lower CO selectivity than the co-feed reactor.

6.4.2 Effect of oxygen flow rate.

With the same porous membrane reactor setup as described above, methane coupling experiments were conducted with 2.6 grams Mn-W-Na/SiO₂ catalyst. Figure 6-7 and Figure 6-8 show the C₂ selectivities and yields as functions of methane conversion for the membrane and co-feed reactors at 805°C and methane and helium flow rates of 5.0 and 120 cc/min respectively. The methane conversions of both membrane and co-feed reactors were varied by changing the oxygen flow rates, while the temperature, methane flow rate, and helium flow rate were kept the same.

Figure 6-7. Comparison of C₂ selectivities in a membrane and co-feed reactor as functions of methane conversion

Figure 6-8. Comparison of C₂ yields in a membrane and co-feed reactor as functions of methane conversion

It can be seen from Figure 6-7 that, for both membrane reactor and co-feed reactor, the C₂ selectivities decrease with the increase of methane conversions. For methane conversions higher than 45%, the membrane reactor gave about 3% higher C₂ selectivity and C₂ yield than those of the co-feed reactor.

Compared to the results obtained under different helium flow rates and fixed methane and oxygen flow rates, there was less improvement of C₂ selectivity and yield at the same methane conversion when a membrane reactor was used. In a membrane reactor, the reaction rate is slower than that in a co-feed reactor due to the segregation of the reactants (methane and oxygen). Therefore, to reach the same methane conversion, a membrane reactor has to be operated at higher oxygen partial pressure, which will result

in lower C_2 selectivity. If the comparisons were to be made at the same methane to oxygen ratio, the differences in C_2 selectivity between the membrane reactor and the co-feed reactor would be greater than those shown in these figures.

Figure 6-9. Comparison of product selectivities in a membrane and co-feed reactor as functions of methane conversion

The product distributions of the two reactors as functions of methane conversion are shown in Figure 6-9. In the whole range of methane conversion shown in Figure 6-9, the membrane reactor showed higher ethylene selectivity than that of the co-feed reactor, while the ethane selectivities were about the same. At low methane conversions, the CO₂ selectivities in the membrane reactor were higher whereas at high methane conversions, the CO selectivities in the membrane reactor were higher than those observed in the co-feed reactor.

Figure 6-10. C₂ selectivities in a membrane reactor as functions of methane conversion

Figure 6-10 and Figure 6-11 show the C₂ selectivities and yields as functions of methane conversion in the membrane reactor at 810°C. The methane conversion was varied by changing the oxygen flow rate. Increasing the helium flow rate from 60 cc/min (open diamonds) to 120 cc/min (solid circles) resulted in a 2-3% increase in both C₂ selectivity and C₂ yield. However, when the methane flow rate was varied from 5.0 cc/min (solid circles) to 3.9 cc/min (crosses), no significant changes in the reactor performance were observed.

The highest C₂ yield obtained in the membrane reactor was 27.5%. This is the highest value for OCM in membrane reactors reported in the literature so far.

Figure 6-11. C₂ yields in a membrane reactor as functions of methane conversion

Chapter 7. Mathematical Modeling

7.1 Analysis and optimization of cross-flow reactors with staged feed policies

7.1.1 Introduction

In many chemical processes, cross-flow reactors [122] can be used to improve the reactor performance over that of conventional tubular reactors by changing the numbers, locations, and amounts of the distributed feed and distributed take-off streams along the reactor length, according to the kinetics of the reaction system. Aris [123] studied the optimization of the bypass and cold stream flow rates in a multistage reaction system by using the dynamic programming technique. Grutter and Messikommer [124] applied dynamic programming to determine the optimal distribution of residence times of an N-stage CSTR chain reactor system. An algorithm was presented by Dyson and Horn [125] to determine the minimum mass of catalyst required by an N-stage adiabatic tubular reactor with feed preheater and direct intercooling by cold feed bypass for the single exothermic reaction with arbitrary kinetics. Jackson [126] proposed an algebraic structure for a network of parallel tubular reactors and sink and source streams. Another reactor network representation was presented by Kokossis and Floudas [127, 128] that has embedded various types of reactors based on CSTRs and PFRs for both isothermal and non-isothermal systems. The solution of the resulting mixed-integral non-linear programming problem gives the optimal configuration of the reactor network.

As the numbers of feed and sink points approach infinity, the cross-flow reactor approaches a membrane reactor. Catalytic inorganic membrane reactors, along with homogeneous catalysis and zeolites, is considered to be one of the three most promising fields in industrial catalysis. Harold et al. [129] described the working concepts of several successful applications of catalytic inorganic membranes and discussed how the membrane reactors could achieve better performance than the conventional reactors. Bernstein and Lund [130] investigated intermediate product yield improvement by using a membrane reactor for series

and series-parallel heterogeneous catalytic reactions. One of the most widely studied membrane reactors is the cross-flow reactor in which only sink points for one of the products are present along the reactor length, such as the Pd-Ag membrane reactor for dehydrogenation [131], where conversions can be achieved which exceed the equilibrium conversion obtained under the same reactant feed conditions in a plug-flow reactor.

Another type of simplified configuration of the cross-flow reactor is one without sinks, in which one of the reactants is fed through injection points along the reactor length. The limiting case of this type of reactor as the number of feeds approaches infinity will be a tube-and-shell reactor with a wall permeable only to the reactant fed from the opposite side of the reactor to the other reactants. Van de Vusse and Voetter [132] determined the optimal concentration gradients in tubular reactors with two feed components by introducing one of the components along the reactor tube. Optimizations were carried out for different reaction rate ratios on an analog computer and compared with those with one-stage tubular reactors. However, only the continuous feed mode was considered in their study and the overall feed ratio of the two reactants was kept as unity. Using the dynamic programming method, Messikommer [133] studied the optimization of semi-continuous chemical reactors on an analog computer.

Reyes et al. [134] developed a detailed kinetic-transport model for methane coupling. They found that staging the introduction of oxygen along the reactor length minimized secondary oxidation reactions and led to a slight increase in product yield. Harold et al. [135] presented a simple model to examine the performance of a supported catalytic membrane with consecutive-parallel reaction system. From a closed-form solution they showed that segregation of the two reactants to opposite sides of the membrane is an effective strategy for increasing the yield of desired product. However, in neither of these two studies did they maximize the product yield by adjusting the overall feed ratio of the two reactants, or any of the model parameters.

A general cross-flow reactor model is developed in this study. The cross-flow reactors were analyzed in terms of residence time, reaction order, and rate constant. Six different types

of feeding modes were compared at their optimal feed distributions or overall feed ratios determined by maximizing the desired product yield at the reactor outlet.

7.1.2 Model development

7.1.2.1 Assumptions

The derivation of the model equations is based on the following assumptions: a) The reactor configuration simulated in this study is a one-dimensional tubular reactor and there is no axial dispersion. All the species involved are ideally mixed radially and thus there are no radial concentration gradients in any cross section of the tubular reactor. b) Reactors are operated at isothermal and isobaric conditions throughout the reactor volume. This implies that both the temperature and total pressure gradients are negligible. c) The reactions may take place either in gas phase or low concentration liquid phase. d) All the reactions involved are irreversible and subject to kinetic control. Therefore, there are no thermodynamic limitations on the reactions. e) Only one of the reactants is fed along the length of the reactor and all the other reactants and inerts are fed at the inlet.

7.1.2.2 Basic equations

A parallel-series reaction scheme is considered in this study, which consists of three irreversible reactions:

where A and B are reactants, P is the desired product, S is the undesired product, and C is the by-product.

The above reaction network structure considered in this study is of practical

importance, and it represents many chemical reaction processes, such as hydrocarbon partial oxidation, hydrogenation and chlorination. For example, in the partial oxidation of hydrocarbons, the desired products such as aldehydes, alcohols, or carboxylic acids can be converted to undesired products such as CO and CO₂. The realization of higher yield and selectivity toward the desired product and the avoidance of the total oxidation is critical to these processes.

Most of the reactions in this type of network are essentially irreversible. The power-law type rate equations have often been assumed for non-catalytic reactions as well as catalytic reactions for simplification. Although any type of reaction rate expression may be inserted into the cross-flow reactor model, the discussion here will be focused on power-law type kinetics. That is to say, the dependencies of the reaction rates on concentration are expressed by the following equations:

$$r_1 = k_1 C_A^{a_1} C_B^{b_1} \quad (7.4)$$

$$r_2 = k_2 C_A^{a_2} C_B^{b_2} \quad (7.5)$$

$$r_3 = k_3 C_P^{a_3} C_B^{b_3} \quad (7.6)$$

If b_1 is less than, equal to, or greater than b_2 and b_3 , we will call the kinetics favorable, neutral, and unfavorable respectively. If reactant B is fed gradually along the length of the reactor, then the dependence of the yield of the desired product, x_1 , and the yield of the undesired product, x_2 , on the dimensionless reactor volume, t , can be related by the following two ordinary differential equations:

$$\frac{dx_1}{dt} = \frac{\sigma_1(1-x_1-x_2)^{a_1}(\theta_B - v_1x_1 - v_2x_2)^{b_1}}{(1+\theta_B+\theta_I+\delta_1x_1+\delta_2x_2)^{a_1+b_1}} - \frac{\sigma_3(v_3x_1)^{a_3}(\theta_B - v_1x_1 - v_2x_2)^{b_3}}{(1+\theta_B+\theta_I+\delta_1x_1+\delta_2x_2)^{a_3+b_3}} \quad (7.7)$$

$$\frac{dx_2}{dt} = \frac{\sigma_2(1-x_1-x_2)^{a_2}(\theta_B - v_1x_1 - v_2x_2)^{b_2}}{(1+\theta_B+\theta_I+\delta_1x_1+\delta_2x_2)^{a_2+b_2}} + \frac{\sigma_3(v_3x_1)^{a_3}(\theta_B - v_1x_1 - v_2x_2)^{b_3}}{(1+\theta_B+\theta_I+\delta_1x_1+\delta_2x_2)^{a_3+b_3}} \quad (7.8)$$

The yields of desired and undesired products are defined by the fraction of reactant A consumed in the formation of product P and S, respectively:

$$x_1 = \frac{F_P}{v_3 F_{Ao}} \quad (7.9)$$

$$x_2 = \frac{F_S}{v_4 F_{Ao}} \quad (7.10)$$

The dimensionless reactor volume, t , is the ratio of the variable volume (V) to the total volume of the reactor (V_R).

$$t = \frac{V}{V_R} \quad (7.11)$$

The integral feed ratio θ_B in Equations 7.7 and 7.8, a function of dimensionless reactor volume, is equal to the ratio of the total number of moles of reactant B introduced into the reactor from $t=0$ (first feed point) to $t=t$ (n -th feed point) to the number of moles of reactant A fed at the inlet of the reactor, or

$$\theta_B = \frac{\sum_{i=1}^{i=n(t=t)} F_{B_i}}{F_{Ao}} \quad (7.12)$$

and θ_I is the inlet mole feed ratio of inerts I to reactant A. δ_1 and δ_2 are the net mole number changes in reactions 1 and 2:

$$\delta_1 = (v_3 + v_5) - (1 + v_1) \quad (7.13)$$

$$\delta_2 = (v_4 + v_6) - (1 + v_2) \quad (7.14)$$

and σ_1 , σ_2 , and σ_3 are dimensionless numbers defined by

$$\sigma_i = k_i \tau_{A0} C_T^{a_i+b_i} \quad (i = 1, 2, 3) \quad (7.15)$$

where C_T is the total concentration, which is equal to $p/(RT)$ for ideal gases, and τ_{A0} the residence time based on reactant A as

$$\tau_{A0} = \frac{V_R}{F_{A0}} \quad (7.16)$$

For a given reactor operated at fixed temperature and pressure, σ_i is dependent only on τ_{A0} and we shall call σ_i the dimensionless residence time with respect to the i -th reaction.

7.1.2.3. Feed policies

First we need to define a feed distribution function for species i

$$\rho_i(t) = \frac{1}{F_{A0}} \lim_{\Delta t \rightarrow 0} \frac{\sum_{j=1}^{j=n'(t=t+\Delta t)} F_{ij} - \sum_{j=1}^{j=n(t=t)} F_{ij}}{\Delta t} \quad (7.17)$$

F_{ij} in the above equation is the molar flow rate of species i fed into the reactor at the j -th feed point. The physical meaning of this feed distribution function is that the quantity $F_{A0}\rho_i(t)\Delta t$ represents the moles of species i introduced into the reactor between reactor volume t and $t+\Delta t$ per unit time. Since reactant A is always fed at the inlet of the tubular reactor ($t=0$) for all the reactor configurations considered in this study, the feed distribution function of A and inerts can be expressed by Dirac delta functions as

$$\rho_A(t) = \delta(t) \quad (7.18)$$

$$\rho_I(t) = \theta_I \delta(t) \quad (7.19)$$

The integral feed ratio, θ_B , in Equations 7.7 and 7.8 can be calculated by integrating the feed distribution function of B, $\rho_B(t)$, from $t=0$ to $t=t$.

$$\theta_B = \int_0^t \rho_B(t) dt \quad (7.20)$$

Six types of feed policies are considered in this study according to the feed policies of the reactant B, and are illustrated in Figure 7-1. Reactant A is not shown in the figure since it is always fed at one end of the reactor. As shown in Figure 7-1 and by their feed distribution expressions given below, the six types of reactors are physically and mathematically interrelated. Type 6 is the most general form and it degenerates to any of the other five types of reactors under certain conditions. For example, it becomes Type 5 when the feed points are equally spaced, turns into Type 4 as the number of feed points approaches infinity, and reduces to Type 1 if there is only one feed point at the inlet of the reactor.

Figure 7-1. Six types of feed policies of reactant B and their interrelations (The numbers labeled refer to the reactor types. N is the number of feed points.)

The continuous supply of reactant B could be achieved either with a porous membrane or with a dense membrane only permeable to reactant B. The optimal feed of reactant B can be realized by changing the membrane wall thickness, pore size, or porosity along the porous membrane tube. In the case of dense membrane, this can be accomplished by changing the wall thickness, composition, or surface properties axially. The loss of reactant and product in a porous membrane reactor can be greatly reduced by maintaining a sufficiently high pressure drop across the membrane [116, 136].

Generally speaking, two functions are required to specify the feed distribution of reactant B: the position function $\psi(t)$ and the magnitude function $\phi(t)$. Position function $\psi(t)$ specifies the N feed positions for reactant B along the reactor tube

$$t_i = \psi\left(\frac{i-1}{N}\right) \quad (i = 1, 2, \dots, N) \quad (7.21)$$

The feed distribution function of B is a discrete function made up of $\phi(t)$ and $\psi(t)$.

$$\rho_B(t) = \sum_{i=1}^N \phi(t) \delta\left[t - \psi\left(\frac{i-1}{N}\right)\right] \quad (7.22)$$

From Equation 7.20 the integral feed ratio is

$$\theta_B = \sum_{i=1}^n \phi\left[\psi\left(\frac{i-1}{N}\right)\right] \quad (7.23)$$

where the step function n is defined by

$$n = i, \quad \text{if } t_i \leq t < t_{i+1} \quad (i = 1, 2, \dots, N-1) \quad (7.24)$$

$$n = N, \quad \text{if } t_N \leq t \leq 1 \quad (7.25)$$

The expressions for the feed distribution function and the integral feed ratio of B for all the six types of feed policies can be derived from the general Equations 7.22 and 7.23, and are

listed in Table 7.1.2.1.

Table 7.1.2.1. Distribution functions and integral feed ratios of reactant B

No	Feed Policies	Feed Distribution Function, ρ_B	Integral Feed Ratio, θ_B	Notes
1	single-stage	$\theta_{Bo} \delta(t)$	θ_{Bo}	$\theta_{Bo} = \theta_B _{t=1}$ $i = i, \text{ if } \frac{i-1}{N} \leq t < \frac{i}{N}$ $(i = 1, 2, \dots, N)$ $n = N, \text{ if } t = 1$
2	uniformly distributed, continuous	θ_{Bo}	$\theta_{Bo} t$	
3	equally spaced and distributed, discrete	$\frac{\theta_{Bo}}{N} \sum_{i=1}^N \delta(t - \frac{i-1}{N})$	$\theta_{Bo} (\frac{n}{N})$	
4	arbitrarily distributed, continuous	$\phi(t)$	$\int_0^t \phi(u) du$	$\phi \geq 0$ $n = i, \text{ if } t_i \leq t < t_{i+1}$ $(i = 1, 2, \dots, N-1)$ $n = N, \text{ if } t_N \leq t \leq 1$ $t_i = \psi(\frac{i-1}{N})$
5	equally spaced and arbitrarily distributed, discrete	$\sum_{i=1}^N \phi(t) \delta(t - \frac{i-1}{N})$	$\sum_{i=1}^n \phi(\frac{i-1}{N})$	
6	arbitrarily spaced and arbitrarily distributed, discrete	$\sum_{i=1}^N \phi(t) \delta[t - \psi(\frac{i-1}{N})]$	$\sum_{i=1}^n \phi[\psi(\frac{i-1}{N})]$	

The introduction of the integral overall feed ratio θ_B as well as the position function ψ and the magnitude function ϕ greatly simplified the simulation of reactors with discrete feed streams. The introduction of the integral overall feed ratio in the derivation of the basic equations enabled the use of only one single material balance equation for each species over the entire length of the discrete feed reactors. So there was no need to apply material balances separately to each section of the reactor between two adjacent feed points. As a result of the representation of the integral overall feed ratio by three functions ϕ , ψ , and n as in Equation 7.23, the simulation and optimization of tubular reactors with discrete feed streams became much simpler and easier, especially for the cases where the number of feed points was very large.

7.1.3 Feed distribution optimization

A reasonable comparison of performance between different types of reactors should be made under their individual optimal conditions. As an optimization criterion, the objective function chosen in the optimization of the feed distribution function was the yield of desired product at the outlet of the reactor.

For Types 1, 2, and 3 reactors operated at a given residence time and for a given set of kinetic parameters, the derivatives of x_1 and x_2 with respect to t in the system equations (Equation 7.7 and 7.8) can be expressed by functions of x_1 , x_2 , t , and θ_{Bo} .

$$\frac{dx_1}{dt} = f_1(x_1, x_2, t, \theta_{Bo}) \quad (7.26)$$

$$\frac{dx_2}{dt} = f_2(x_1, x_2, t, \theta_{Bo}) \quad (7.27)$$

For these three types of reactors only the overall feed ratio θ_{Bo} , rather than the distribution function needs to be optimized. Suppose that the solutions of the above equations are

$$x_1 = F_1 (t, \theta_{Bo}) \quad (7.28)$$

$$x_2 = F_2 (t, \theta_{Bo}) \quad (7.29)$$

Then the objective function F is

$$F = F_1 (1, \theta_{Bo}) \quad (7.30)$$

or

$$F = F (\theta_{Bo}) \quad (7.31)$$

The optimal overall feed ratio, θ_{Bo}^* , would be the value at which the function F is maximized,

$$F_{\max} = F (\theta_{Bo}^*) \quad (7.32)$$

For Types 4, 5, and 6 reactors, it is necessary to determine the feed distribution function $\rho_B(t)$, which is a function of two functions $\phi(t)$ and $\psi(t)$. Assume that both ϕ and ψ can be expressed by a certain type of function (a polynomial, say) as

$$\phi = \phi (t, s_1, s_2, \dots, s_{ND}) \quad (7.33)$$

$$\psi = \psi (t, s_{ND+1}, s_{ND+2}, \dots, s_{ND+NP}) \quad (7.34)$$

where all the s_i ($i = 1, 2, \dots, ND+NP$) are the coefficients to be optimized and ND and NP are the number of coefficients appearing in functions ϕ and ψ respectively. By doing so, the original dynamic optimization becomes a static optimization problem. Then the system equations for these three types of reactors can be expressed by

$$\frac{dx_1}{dt} = f_1 (x_1, x_2, \phi, \varphi) \quad (7.35)$$

$$\frac{dx_2}{dt} = f_2 (x_1, x_2, \phi, \varphi) \quad (7.36)$$

and their solutions by

$$x_1 = F_1 (t, s_1, s_2, \dots, s_{ND}, s_{ND+1}, s_{ND+2}, \dots, s_{ND+NP}) \quad (7.37)$$

$$x_2 = F_2 (t, s_1, s_2, \dots, s_{ND}, s_{ND+1}, s_{ND+2}, \dots, s_{ND+NP}) \quad (7.38)$$

The optimal feed distribution function, ρ^*_B (or ϕ^* and ψ^*) would be the one with which the function F_1 is maximized. Specifically, we are searching for the optimal values of the ND+NP coefficients, or for the maximum of function F_1

$$F_{\max} = F_1 (1, s_1^*, s_2^*, \dots, s_{ND}^*, s_{ND+1}^*, s_{ND+2}^*, \dots, s_{ND+NP}^*) \quad (7.39)$$

7.1.4 Algorithm

Substituting the integral feed ratio θ_{B_0} into Equations 7.7 and 7.8, one will obtain the system equations for each of the six types of reactors associated with their feed policies of reactant B. Then the system equations are integrated by fourth order Runge-Kutta Method with adaptive stepsize control. By making frequent changes in the step-size during integration, a predetermined accuracy in the solution with minimum computational effort can be achieved. In the determination of the overall feed ratio θ_{B_0} for feed policies of types 1, 2, and 3, the Golden Section Search Method was used. Other methods such as Newton's Method, cannot be used due to the fact that the desired product yield, x_1 , is an implicit function of θ_{B_0} and that, for feed policy 3 this function is not differentiable. The Hooke-Jeeves Method [137] was employed to find the optimal feed distribution functions (or the coefficients s_i , $i=1,2,\dots,ND+NP$) for feed policies 4, 5, and 6. This method does not require the derivatives of x_1 (desired product yield) with respect to the variables to be optimized. Although the computing time needed by this method is relatively long, especially for the cases where more variables are involved and the speed of convergence is slower near the maximum point, it has very good stability and adaptability.

7.1.5 Results and discussion

Before discussing the simulations, we need to define the conversion, yield and selectivity properly. Of the two reactants, A is considered to be the more expensive material. Therefore the conversion, selectivity and yield are defined based on reactant A. Accordingly, conversion $x(t)$ is the fraction of the amount of initially introduced reactant A that is consumed from $t=0$ to t . Product yield $x_i(t)$ is the fraction of the amount of reactant A initially introduced that is converted to product i . For the reaction system as shown in Equations 7.1-7.3, the conversion is equal to the sum of the yields of desired and undesired products or $x(t)=x_1(t)+x_2(t)$. Selectivity $s_i(t)$ is the ratio of the amount of A consumed for the production of product i to the total amount of A converted.

7.1.5.1 Effect of kinetic order on the performance of evenly spaced and equally distributed staged feed reactors

Since the tubular reactors considered in this study are those in which reactant A is fed at the inlet, the concentration profile of reactant A cannot be changed independently. The objective of the study is to look at the effect of the feed policy of reactant B on reactor performance. Thus in the following discussion the kinetic order with respect to reactant A is fixed. Here we choose $a_1=a_2=a_3=1$, and the stoichiometric coefficients $v_i=1$ ($i=1,2,\dots,6$) (therefore $\delta_1=0$ and $\delta_2=0$). Figures 7-2 - 7-4 show the dependence of desired product yield on dimensionless residence time for staged feed reactors (type 3 for general N , type 2 when $N=\infty$, and type 1 when $N=1$) with three different kinetics. The other kinetic and operation parameters are listed in Table 7.1.5.1.

Table 7.1.5.1. Kinetic parameters used in Figures 7-2 to 7-4

Kinetics	Favorable	Neutral	Unfavorable
Figure	Figure 7-2	Figure 7-3	Figure 7-4
Parameters	$\sigma_1:\sigma_2:\sigma_3=1:10:10$ $b_1=1, b_2=2, b_3=2$	$\sigma_1:\sigma_2:\sigma_3=1:1:1$ $b_1=1, b_2=1, b_3=1$	$\sigma_1:\sigma_2:\sigma_3=10:1:1$ $b_1=2, b_2=1, b_3=1$

For favorable parallel kinetics as shown in Figure 7-2, since the distributed feed of B causes a lower concentration of B, an increase either in the number of feed points or residence time will help to decrease the concentration of reactant B. So, both selectivity and yield of the desired product increase with the number of feed points and residence time and the membrane reactor, where the number of feed points is equal to infinity, gives the highest selectivity and yields at its optimal overall feed ratio. In the low σ_1 region, where the residence time is short and the conversion is low, the effect of distributed feed of B has only a small effect on the performance of the reactors and all the reactors give nearly the same selectivity and yield as the single stage co-feed reactor. This suggests that with favorable kinetics, a sufficiently large σ_1 value is required by the staged feed reactors to realize significantly higher product yields than a co-feed reactor.

Figure 7-2. Effect of residence time on the maximum product yield of staged-feed reactors with favorable kinetics

Since the ratios of reaction rate constants σ_1 , σ_2 and σ_3 in Figure 7-2 are set at 1:10:10, the value of σ_1 is a measure of residence time of the reactors. According to the above results in the low residence time region with favorable kinetics, the optimal overall feed ratios for staged feed reactors increase as the number of feed points increases. But the maximum desired product yield at the outlet decreases. This means that the reactors with more feed points require more reactant B than those with fewer feed points since they operate at higher overall feed ratios but give lower yield than the co-feed reactor. It can be concluded that even with favorable kinetics distributed feed reactors are not as good as co-feed reactors at low σ_1 conditions. From Figure 7-2, it is clear that only at higher σ_1 values do staged feed policies show their advantages over co-feed reactors and 100 % desired product yield could be realized when both the stage number and residence time approach infinity.

The simulation results for neutral kinetics are shown in Figure 7-3. Since the dependence of reaction rates on the concentration of reactant B is the same both for desired and undesired reactions, the suppression of the concentration of B by staged feed policies has no favorable effect on the desired product. Therefore, as indicated by Figures 7-3 and 7-4, essentially there is no difference in performance between reactors with different feed points.

A plot of maximum yield of a membrane reactor (Type 2 reactor) versus that of a co-feed reactor with σ_1 as the third parameter is given in Figure 7-5. The undesired reaction orders in the distributed reactant, b_2 and b_3 , were changed over the range of 0.55 to 5, while the other reaction orders were kept constant ($a_1, a_2, a_3 = 1.0, b_1 = 0.5$). Since the ratios of σ_2/σ_1 and σ_3/σ_1 were fixed in Figure 7-5, σ_1 is proportional to the residence time.

Again higher residence time resulted in larger yield differences between membrane reactor and co-feed reactor. As the undesired reaction orders increase, the yields of both membrane and co-feed reactors increase. However, depending on the contact time, the yield difference begins to decrease after the undesired reaction orders reach a certain value, although the membrane reactor always gives higher desired product yield than the co-feed

reactor except in the low residence time region, which will be discussed later.

Figure 7-3. Effect of residence time on the maximum product yield of staged-feed reactors with neutral kinetics

Figure 7-4. Effect of residence time on the maximum product yield for staged-feed reactors with different numbers of feed points for unfavorable kinetics

Figure 7-5. Effect of undesired reaction orders on the maximum yield

7.1.5.2. Effect of reaction rate constants on the performance of evenly spaced and equally distributed reactors for favorable kinetics

As discussed above, it is the staged feed policy of reactant B that may offer higher desired product yield than the single-stage feed policy. Also the residence time needs to be high enough for a staged feed reactor to make a significant improvement in the yield obtained by the one-stage co-feed reactors. The effect of reaction rate constants on the reactor performance will be investigated next. Figures 7-6 to 7-8 show the optimal overall feed ratio, selectivity, and maximum yield as a function of σ_1 for σ_2 and $\sigma_3 = 1, 10$, and 100 for favorable kinetics with the following kinetic parameters: $a_1 = a_2 = a_3 = b_1 = 1, b_2 = b_3 = 2$.

Figure 7-6. Dependence of optimal overall feed ratio on reaction rate constants (solid lines: co-feed reactor; dashed lines: 2-stage-feed reactor; dash-and-dot lines: membrane reactor.)

Figure 7-7. Dependence of desired product selectivity at optimal overall feed ratio on reaction rate constants

Figure 7-8. Dependence of the maximum product yield on reaction rate constants

Since σ_2 and σ_3 are fixed for each curve, the variation in σ_1 can be interpreted as the variation in the desired reaction rate constant, k_1 . Likewise for a fixed σ_1 , the variation in σ_2 and σ_3 among different curves can be interpreted as the variation in the rate constants of the parallel and series reactions. For the same σ_1 value, kinetics with lower σ_2 and σ_3 values require a higher overall feed ratio of B to A than those with higher σ_2 and σ_3 values, because the relative rates of undesired reactions are slower and the increase of B in the feed will favor the desired reaction (see Figure 7-7). As the desired reaction rate (or σ_1) increases, the product yield approaches unity (Figure 7-8) and further increase of B will result in less product produced than consumed by the series reaction since the product formed greatly outnumbers the reactant A left over. Consequently, the optimal overall feed ratio drops with a limit of stoichiometric coefficient ratio (unity) as the desired reaction rate increases. Again, as shown in Figure 7-8, only in the high σ_i ($i=1, 2$, and 3) range does the membrane reactor offer significant improvement in the maximum yield over the co-feed reactor.

A comparison of maximum yields in σ space for the co-feed reactor and the membrane reactor (Type 2 reactor) with the same favorable kinetics as in Figures 7-6 to 7-8 is depicted in Figure 7-9. For any reaction system with given σ_2/σ_1 and σ_3/σ_1 , the σ_1 -curve gives the value of σ_1 for which the membrane reactor gives the same maximum product yield as the co-feed reactor. On the left side of the σ_1 curve, the co-feed reactor gives higher maximum product yield; while on the right side of the σ_1 curve, the membrane reactor gives higher maximum product yield. The whole σ space can be divided into four regions: Regions I, II, III, and IV. In the whole σ space, an increase in either σ_1 or in σ_2/σ_1 results in an increase in the difference of maximum yield between membrane reactor and co-feed reactor, or

$$\left(\frac{\partial \Delta x}{\partial \sigma_1} \right)_{\sigma_2/\sigma_1, \sigma_3/\sigma_1} > 0 \quad (7.40)$$

$$\left(\frac{\partial \Delta x}{\partial \sigma_2} \right)_{\sigma_1, \sigma_3} > 0 \quad (7.41)$$

where Δx is the maximum yield difference between the membrane reactor and co-feed reactor

$$\Delta x = x_1^{mem} - x_1^{cof} \quad (7.42)$$

Δx is positive if $(\sigma_2/\sigma_1, \sigma_3/\sigma_1)$ is on the right of the σ_1 curve and negative if on the left.

In Region I, σ_2/σ_1 is so small that the reaction system essentially becomes a series one while in Region IV, where σ_3/σ_1 is very small, the reaction system is parallel. Between Region I and IV, there are two regions divided by a dashed curve, on which the derivative of Δx with respect to σ_3 is equal to zero,

Figure 7-9. Comparison between co-feed and membrane reactors in σ space

$$\left(\frac{\partial \Delta x}{\partial \sigma_3} \right)_{\sigma_1, \sigma_2} = 0 \quad (7.43)$$

On the left side of the dashed curve (regions I and II), the difference in maximum yield, Δx , increases with σ_3/σ_1 , while on the right side (regions III and IV), Δx decreases with σ_3/σ_1 .

7.1.5.3 Comparison of performances among the six types of reactors for favorable kinetics

So far results have been presented for the first three types of reactors, which are evenly distributed staged feed reactors. From the results shown above, it is clear that only with favorable kinetics do the staged feed reactors have advantages over the conventional plug flow reactor. From now on, therefore, the study will focus on favorable kinetics only.

For Types 4 and 5, the function ϕ must be optimized. For the unevenly distributed continuous reactor (Type 4), this function represents the distribution function, whereas for discrete unevenly distributed reactors (Type 5 and Type 6) ϕ refers to the feed ratio of B to A. If function ϕ is expressed by a polynomial of dimensionless reactor volume t with ND adjustable parameters as

$$\phi(t) = \sum_{i=1}^{ND} s_i t^{i-1} \quad (7.44)$$

then the integral overall feed ratio, θ_{Bo} , of Type 4 reactor will be

$$\theta_B = \sum_{i=1}^{ND} \frac{s_i}{i} t^i \quad (7.45)$$

If no reactant will be fed at the end of the reactor, or $\phi(1)=0$, choose ϕ in the form of

$$\phi(t) = (1-t) \sum_{i=1}^{ND} s_i t^{i-1} \quad (7.46)$$

By doing this fewer parameters are required for polynomials of the same order. The integral feed ratio for Type 4 reactor is

$$\theta_B = \sum_{i=1}^{ND+1} \frac{(s_i - s_{i-1})}{i} t^i \quad (7.47)$$

where $s_0 = s_{ND+1} = 0$. For Type 5 reactor

$$\theta_B = \sum_{i=1}^N \left(1 - \frac{i-1}{N} \right) \sum_{j=1}^{ND} s_j \left(\frac{i-1}{N} \right)^{j-1} \quad (7.48)$$

An additional position function, $\psi(t)$, is needed to specify the feed distribution function of the Type 6 reactor. If a polynomial form is chosen again for $\psi(t)$ and it is assumed that the $\psi(t)$ of the Type 6 reactor has the same function values as those of the Type 5 reactor at $t=0$ and 1, or $\psi(0)=0$ and $\psi(1)=1$, then

$$\psi(t) = t \left[1 + \sum_{i=1}^{NP} s_{ND+i} t^{i-1} - \left(\sum_{i=1}^{NP} s_{ND+i} \right) t^{NP} \right] \quad (7.49)$$

and

$$\theta_B = \sum_{i=1}^N (1 - t_i) \sum_{j=1}^{ND} s_j t_i^{j-1} \quad (7.50)$$

where

$$t_i = \frac{i-1}{N} \left[1 + \sum_{i=1}^{NP} s_{ND+i} \left(\frac{i-1}{N} \right)^{i-1} - \left(\sum_{i=1}^{NP} s_{ND+i} \right) \left(\frac{i-1}{N} \right)^{NP} \right] \quad (7.51)$$

Figure 7-10 shows the desired product yield and selectivity as functions of dimensionless residence time for the six types of reactors. It can be seen from the figure that

Figure 7-10. Maximum desired product yield of the six types of reactors as a function of residence time (N is the number of feed points)

at the optimal feed distribution of reactant B or optimal overall feed ratio of B to A, both selectivity (not shown in the figure) and yield of the desired product increase as the number of feed points and dimensionless residence time increase. In addition, the optimal distributed feed policies always result in higher maximum product yield than evenly distributed reactors both for discrete (with same number of feed points) and continuous feed modes. As for the number of parameters used in these two functions, simulation results showed that the maximum yield was not very sensitive to the feed distribution. Therefore, polynomial expressions with about 4 or 5 parameters were enough for most of the conditions covered in the modeling studies.

Figures 7-11 and 7-12 give the axial feed distributions of reactant B for different kinds of reactors operated under the following conditions: $a_1 = a_2 = a_3 = 1$, $b_1 = b_2 = 2$, $\sigma_1 = 100$ and

1000, and $\sigma_1:\sigma_2:\sigma_3 = 1:10:10$. For the unevenly distributed reactors (Type 4, Type 5, and Type 6), more reactant B was introduced into the reactor from the upstream than from the downstream. To keep a relatively low B/A ratio to achieve high selectivity and a sufficiently high overall feed ratio of B/A enough to maintain a reasonable conversion level of reactant A, one needs to feed more reactant B in the region near the inlet, where the concentration of reactant A is higher than that in the downstream. In addition, the concentration of the desired product (P) is higher in the downstream. And higher concentration of reactant B in the downstream will increase the reaction extent of the serial reaction of product with B to form undesired product much more than in the front region of the reactor.

Figure 7-11. Feed distribution functions of continuous supply of reactant B

Figure 7-12. Feed distributions of discrete supply of reactant B through 10 feed points

From the yields shown in Figure 7-11 we see that although the optimal feed distribution of B gives higher product yield than evenly distributed distribution does, the increase in the product yield is not so big as that from co-feed reactor to evenly distributed reactors. This is not a surprise because of the fact that the difference between the feed distribution functions of optimally and equally distributed feed reactors is not as big as that between the evenly distributed reactor and the co-feed reactor, in which the feed distribution function is zero except at the inlet, where the distribution function is infinity. If we compare the feed distributions of Type 4, Type 5, and Type 6 reactors at $\sigma_1=100$ and 1000, the distributions of reactant B at $\sigma_1=1000$ were steeper than those at $\sigma_1=100$. At higher σ_1 values, since the reactions proceed faster, more reactant A is converted in the early part than in the latter part of the reactor. Thus more reactant B is required in the upstream than in the

downstream.

7.1.3.6 Summary

A general cross-flow reactor model with six types of feeding modes has been developed. Maximum desired product yields achieved by reactors between different feeding modes were compared under their optimal overall feed ratio or feed distribution conditions. In order for the distributed reactor to achieve higher desired product yield than the conventional co-feed reactor, the reaction order in the distributed-feed reactant of the desired reaction must be lower than those of the undesired reactions. The quantities of the residence time multiplied by the rate constants of the reactions involved should be within in certain regions. The parametric study provides guidance for the evaluation of the effectiveness of using multiple-staged feed reactors and membrane reactors to improve the reactor performance in terms of kinetic parameters (reaction orders and rate constants) and operating parameters (residence time, temperature and pressure).

7.2 Analysis and optimization of cross-flow reactors for oxidative coupling of methane

7.2.1 Introduction

Since the pioneering work of Keller and Bhasin [36], there has been tremendous interest in the oxidative coupling of methane to C_2 hydrocarbons, and extensive R&D efforts in this area have been made [3, 12, 14, 31, 32, 33, 35, 41, 52]. It was estimated that a single-pass conversion of 35~37% and selectivity of 85~88% (equivalent to 30+% C_2 yield) are required to achieve commercial feasibility [42, 43]. High C_2 yield can be achieved by increasing methane conversion, C_2 selectivity, or both. Unfortunately, higher selectivity is usually obtained at lower conversion. Most of the effort devoted to the study of oxidative coupling of methane so far has been in catalyst characterization, reaction mechanism and catalyst screening. By now the periodic table has been visited extensively in catalyst screening

studies, but the C_2 yields achieved are still less than 30%.

Examination of the reaction orders in oxygen and methane in the kinetic expressions for different OCM catalysts reported in the literature [43, 105, 106, 107, 108, 109, 110, 111, 112, 113, 114, 115] showed that, except for the data by Bartsch et al. [104], the reaction order with respect to methane for C_2 formation is always higher than that for CO_x formation, while the reaction order with respect to oxygen for C_2 formation is always lower than that for CO_x formation. This means that reactor configurations that maintain a high ratio of methane to oxygen concentration throughout the reactor should favor the desired C_2 formation reaction. The same conclusion may also be obtained by a thermodynamic analysis, that the relative amount of C_2 to CO_x increases with methane to oxygen ratio. Possible reactor configurations include a reactor with oxygen introduced at discrete feed points along the reactor length, and a membrane reactor with the wall of the membrane as a continuous oxygen distributor.

The first experimental study showing the beneficial effect of distributed oxygen feed on methane conversion and C_2 selectivity was done by Choudhary et al. [49] in tubular reactors connected in series with La/MgO as the catalyst. For a fixed overall ratio of methane to oxygen, the C_2 yield increased as the number of oxygen feed points increased. Similar results were obtained by Santos et al. [79], that with an appropriate choice of reaction conditions the yields obtained with the distributed feed reactor were found to be higher than those with a single feed reactor. A three-stage reactor packed with Li/MgO catalyst was used by Matsura and Yoshida [80] to improve yield and 49% methane conversion and 60% C_{2-2} hydrocarbon selectivity were obtained. Mleczko et al. [81] studied both fixed and fluidized-bed reactors operated in two different modes: co-feed of CH_4 and O_2 and distributed feed of O_2 with three catalysts: $PbO/\gamma-Al_2O_3$, $NaOH/CaO$, and La_2O_3/CaO . The distributed feed resulted in a marked increase of selectivity and yield. However, in another paper [102], it was claimed that, when the operation mode of distributed oxygen feed was applied, no improvement of C_2 selectivity and yield compared to co-feed operation was achieved, and they concluded that the effectiveness of the distributed feed of oxygen depended mainly on

the applied catalyst. A comparison study of various types of reactors for OCM by Do et al. [82] showed that for the same total input of oxygen, the performances of a single-stage and a two-stage fluidized-bed reactor with interstage addition of oxygen were the same for different catalysts over a wide range of reaction conditions. Campbell and Ekstrom [83] carried out OCM with a five-stage distributed oxygen feed reactor and they did not conclude that distributed oxygen feed could significantly improve the C_{2+} yield. Methane oxidative coupling in porous alumina membrane reactors prepared by modifying the porous alumina membrane with silica was studied by Santamaria and co-workers [51a, 51b] and C_2 selectivity higher than the conventional packed-bed reactor was obtained. Ramachandra et al. [116] studied OCM by using a Vycor glass membrane reactor and they found that at the same methane conversion, the membrane reactor gave higher C_2 selectivity than a co-feed packed-bed reactor.

Simulation studies by Santamaria et al. [72, 73] indicate that the distributed oxygen feed may significantly improve the yield to hydrocarbons in the OCM process. Reyes et al. [74] developed a kinetic-transport model including both homogeneous and heterogeneous reactions for methane coupling. Staging the introduction of oxygen along the reactor length minimized the secondary oxidation reaction by lowering the local oxygen partial pressure and led to a slight increase in product yield. Wang and Lin [138] analyzed OCM in dense oxide membrane reactors using a model based on equations that describe OCM kinetics on the membrane surface, oxygen permeation through the membrane, and mass transfer and reactions in a membrane CSTR or PFR. Modeling results show a possibility of achieving much higher C_2 yield (>70%) for OCM in the dense oxide membrane reactors than in the conventional packed-bed reactor. A simulation study by Cheng and Shuai [139] showed that using a catalytic membrane reactor would greatly improve the selectivity and yield to C_2 hydrocarbons, compared with the co-feed operation. Rojnuckarin et al. [140] utilized an optimal control strategy of temperature and flux to improve the yield of chlorine-catalyzed oxidative pyrolysis of methane to ethylene and acetylene. 338 reactions were considered in their study and more than 40% yield was predicted. Unlike the homogeneous catalytic process, the presence of a solid catalyst in the heterogeneous oxidative coupling of methane

could greatly reduce the extent of gas phase reactions and, since less is known about detailed solid-catalyzed kinetics, simpler kinetics have been used in the modeling studies.

An alternative way to increase the C_2 yield of the OCM process is to separate C_2 either by a cryogenic method or by adsorption, and recycle the unconverted methane [43,141,142]. Hall and Myers [143] studied the effects of product separation on the kinetics and selectivity of oxidative coupling of methane. By using a simulated countercurrent moving-bed chromatographic reactor (SCMBCR), Tonkovich et al. [45] reported 50% C_2 yield with Sm_2O_3 as catalyst. This reactor contained four reactor units which maintained a high ratio of methane to oxygen (50:1) and four separation columns to remove the C_2 hydrocarbons from the unreacted methane and oxygen. In another paper [46], an ethylene yield up to 85% and a total C_2 yield up to 88% were achieved in a gas recycle electrocatalytic or catalytic reactor where the recycled gas passed continuously through a molecular sieve trap in the recycle loop. Although the C_2 separation outside the reactor with methane recycle can improve the C_2 yield, the processes involved may be too complicated to be economically feasible. In addition, the C_2 yields achieved by these processes are no longer the single-pass C_2 yield, which has to be higher than 30% to make OCM industrially viable. A membrane reactor with a membrane to selectively remove the C_2 products could combine the reaction and separation in a single unit. This would simplify the process and improve the OCM reactor performance as well.

All of the experimental and modeling studies mentioned above were carried out at the same methane to oxygen ratio or fixed residence time for different types of reactors. Methane to oxygen ratio is an important parameter for the OCM process and only under optimal conditions will the comparison be reasonable and meaningful. Therefore, the comparison of different reactor configurations should be based on the optimal methane to oxygen ratio of each, which is also a function of residence time (or contact time) as well as dilution rate, temperature and pressure. So far, neither optimization in terms of methane to oxygen ratio and oxygen feed distribution nor a study regarding the removal of C_2 in a membrane reactor to achieve higher C_2 yield for OCM has been reported.

In this chapter a systematic modeling study of cross-flow reactors with distributed

feed of oxygen and product removal is presented. The simulation study was focused on the effect of reactor configuration and oxygen feed distribution (rather than the flow pattern, transport properties, and catalyst characteristics, etc.) on the performance of the cross-flow reactors. The reactor configuration simulated in this study was a tubular reactor with methane fed at the inlet and oxygen along the reactor length. Any species may be removed from the reactor through a membrane. Different reactor configurations were compared in terms of maximum C_2 yield, and their overall feed ratios of methane to oxygen or oxygen feed distribution functions were optimized so that the C_2 yield at the outlet of the reactor was maximized.

7.2.2 Modeling

Catalytic oxidative coupling of methane is a complex process and involves both surface and gas phase reactions occurring simultaneously [3, 144, 145]. There is no simple mechanism to describe this homogeneous-heterogeneous reaction system. Due to the high conversion of oxygen and the interaction between homogeneous and heterogeneous reactions, power-law type rate expressions were usually assumed and the kinetic parameters (reaction orders, reaction rate constants, and activation energies) were evaluated by fitting the experimental data.

The performances of the cross-flow reactor depend on the situation of the kinetic equations used in the model. As indicated by our previous modeling study of cross-flow reactor based on general kinetic expressions [146], whether a distributed reactant feed reactor gives better performance than a co-feed reactor mainly depends on the magnitude of reaction order with respect to the distributed reactant (which is oxygen for OCM) for the desired reaction relative to that for the undesired reaction. If the reaction order in the distributed reactant of the desired reaction is lower than that of the undesired reaction, distributed supply of the reactant is beneficial compared to the conventional co-feed reactor. In the case of methane oxidative coupling as mentioned earlier, almost all the kinetic studies with different OCM catalysts showed that the C_2 formation reaction has a lower reaction order in oxygen and a higher reaction order in methane than CO_x (CO and CO_2) formation. Thus, no matter

which kinetic expression is used, the distributed feed of oxygen always gives an advantage over the co-feed reactor. Since the purpose of this study is to optimize the oxygen feed distribution rather than the OCM catalysts, the kinetics of the best catalyst, which are not available in the literature, were not used. As an example, we chose the kinetic equations developed by Hinsien et al. [110] with 34% PbO supported on γ -Al₂O₃. Although PbO/Al₂O₃ is not the best catalyst, Hinsien's kinetics are among the few with complete OCM kinetic expressions available. The kinetics of any of the catalysts for OCM are eligible without losing the generality of the model. In fact, we applied other kinetics such as Tung and Lobban's for Li/MgO [115] and we got similar results because of the reasons explained above.

The experimental conditions for the kinetic studies [110] were varied as follows: $p_{O_2} = 0.027 - 0.13$ bar; $p_{CH_4} = 0.17 - 0.65$ bar; $T = 650, 680, 700, \text{ and } 730$ °C; $W/F (T,P) = 0.0022$ and 0.049 g sec/ml. These kinetics are simple and include the further oxidation of C₂ to CO_x with the following parallel-series reaction scheme:

The rate expressions for the four reactions are

$$r_1 = 1.2 e^{-99000/RT} C_{CH_4}^{0.8} C_{O_2}^{1.1} \quad (7.56)$$

$$r_2 = 2.0 \times 10^{-4} e^{-6000/RT} C_{C_2H_6}^{0.8} C_{O_2}^{1.0} \quad (7.57)$$

$$r_3 = 1.5 \times 10^{-2} e^{-51000/RT} C_{CH_4}^{0.4} C_{O_2}^{1.5} \quad (7.58)$$

$$r_4 = 2.0 \times 10^{-16} e^{220000/RT} C_{C_2H_4}^{0.8} C_{O_2}^{1.6} \quad (7.59)$$

where the gas constant $R=1.987 \text{ J}/(\text{mol K})$ and the units of the reaction rates are $\text{mol}/(\text{g cat sec})$. The negative apparent energy of activation for Reaction 7.55, as interpreted by Hinsien et al. [110], may be understood in such a way that the temperature dependence of this reaction is affected by adsorption thermodynamics.

Figure 7-13 illustrates the general reactor configuration simulated in this study. Methane is fed at the inlet of the reactor along with the inert and oxygen is introduced into the reactor at different feed points along the reactor length. Any species may be removed from the reactor through the reactor wall, according to its permeability. Here are some of the variations that are covered by the general reactor configuration: if oxygen is fed only at the inlet along with methane and there is no product removal, it is reduced to the conventional co-feed reactor; if oxygen is introduced into the reactor at N feed points along the reactor axial position, it is the multiple stage-feed reactor; as the number of feed points N increases toward infinity, it is equivalent to a membrane-feed reactor; if oxygen is fed only at the inlet and some of the products are selectively removed through the reactor wall, it turns into a product-removal membrane reactor; if we feed oxygen through one membrane and also remove product through another membrane, it becomes a two-membrane reactor.

The derivation of the model equations governing the reactors is based on the following assumptions: a) reactors are operated at isothermal and isobaric conditions. b) the

Figure 7-13. General reactor configuration

reactor model is one-dimensional and there is no axial dispersion, and all the species are ideally mixed radially and thus there are no radial concentration gradients in any cross section along the reactor length; c) the reactions take place only in the methane-feed side and there is no chemical reaction in the oxygen feed side or in the permeation side.

The reactor model can be described by the following ordinary differential equations:

$$\frac{dx_1}{dt} = k_1 \tau C_T^{1.9} \delta_{CH_4}^{0.8} \delta_{O_2}^{1.1} / \delta_T^{1.9} - k_2 \tau C_T^{1.8} \delta_{C_2H_6}^{0.8} \delta_{O_2} / \delta_T^{1.8} \quad (7.60)$$

$$\frac{dx_2}{dt} = k_2 \tau C_T^{1.8} \delta_{C_2H_6}^{0.8} \delta_{O_2} / \delta_T^{1.8} - k_4 \tau C_T^{2.4} \delta_{C_2H_4}^{0.8} \theta_{O_2}^{1.6} / \delta_T^{2.4} \quad (7.61)$$

$$\frac{dx_3}{dt} = k_3 \tau C_T^{1.9} \delta_{CH_4}^{0.4} \delta_{O_2}^{1.5} / \delta_T^{1.9} + k_4 \tau C_T^{2.4} \delta_{C_2H_4}^{0.8} \delta_{O_2}^{1.6} / \delta_T^{2.4} \quad (7.62)$$

$$\frac{dx_4}{dt} = \lambda_{C_2H_6} C_T [(x_1 - x_4) / \delta_T - x_4 / \delta_T'] \quad (7.63)$$

$$\frac{dx_5}{dt} = \lambda_{C_2H_4} C_T [(x_2 - x_5) / \delta_T - x_5 / \delta_T'] \quad (7.64)$$

$$\frac{dx_6}{dt} = \lambda_{CO_2} C_T [(x_3 - x_6) / \delta_T - x_6 / \delta_T'] \quad (7.65)$$

$$\frac{dx_7}{dt} = \lambda_{CH_4} C_T [\delta_{CH_4} / \delta_T - x_7 / \delta_T'] \quad (7.66)$$

$$\frac{dx_8}{dt} = \lambda_{H_2O} C_T [(0.5 x_1 + x_2 + 2 x_3 - x_8) / \delta_T - x_8 / \delta_T'] \quad (7.67)$$

$$\frac{dx_9}{dt} = \lambda_{O_2} C_T [\delta_{O_2} / \delta_T - x_9 / \delta_T'] \quad (7.68)$$

$$\frac{dx_{10}}{dt} = \lambda_I C_T [(\theta_I - x_{10}) / \delta_T - (\theta_I' + x_{10}) / \delta_T'] \quad (7.69)$$

where

$$\delta_{O_2} = \theta_{O_2} - 0.25x_1 - 0.5x_2 - 2x_3 - x_9 \quad (7.70)$$

$$\delta_{CH_4} = 1 - x_1 - x_2 - x_3 - x_7 \quad (7.71)$$

$$\delta_{C_2H_6} = 0.5(x_1 - x_4) \quad (7.72)$$

$$\delta_{C_2H_4} = 0.5(x_2 - x_5) \quad (7.73)$$

$$\delta_T = 1 + \theta_{O_2} + \theta_I - 0.25x_1 - 0.5(x_4 + x_5) - x_6 - x_7 - x_8 - x_9 - x_{10} \quad (7.74)$$

$$\delta_T' = \theta_I' + 0.5(x_4 + x_5) + x_6 + x_7 + x_8 + x_9 + x_{10} \quad (7.75)$$

In these equations x_1 , x_2 , and x_3 are the yields of ethane, ethylene, and carbon dioxide, defined by

$$x_1 = 2 (F_{C_2H_6} + F_{C_2H_6}') / F_{CH_4}^0 \quad (7.76)$$

$$x_2 = 2 (F_{C_2H_4} + F_{C_2H_4}') / F_{CH_4}^0 \quad (7.77)$$

$$x_3 = (F_{CO_2} + F_{CO_2}') / F_{CH_4}^0 \quad (7.78)$$

where F_i and F_i' are the molar flowrates of species i in the reaction side and in the permeation side. The quantities x_4 , x_5 , x_6 , x_7 , x_8 , x_9 , and x_{10} are the ratios of molar flow rates of $1/2C_2H_6$, $1/2C_2H_4$, CO_2 , CH_4 , H_2O , O_2 and inerts in the permeation side to the mole flow rate of methane initially introduced at the reactor inlet, respectively.

$$x_4 = 2 F_{C_2H_6}' / F_{CH_4}^0 \quad (7.79)$$

$$x_5 = 2 F_{C_2H_4}' / F_{CH_4}^0 \quad (7.80)$$

$$x_6 = F_{CO_2}' / F_{CH_4}^o \quad (7.81)$$

$$x_7 = F_{CH_4}' / F_{CH_4}^o \quad (7.82)$$

$$x_8 = F_{H_2O}' / F_{CH_4}^o \quad (7.83)$$

$$x_9 = F_{O_2}' / F_{CH_4}^o \quad (7.84)$$

$$x_{10} = F_I' / F_{CH_4}^o \quad (7.85)$$

In the above equations t is the dimensionless reactor length. θ_{O_2} in the model equations is called the integral feed ratio, which is a function of dimensionless reactor length and is equal to the ratio of the total number of moles of oxygen introduced into the reactor from $t=0$ (first feed point) to $t=t$ (n -th feed point), to the number of moles of methane fed at the reactor inlet, or

$$\theta_{O_2} = \sum_{i=1(t=0)}^{i=n(t=t)} F_{O_2,i}' / F_{A0} \quad (7.86)$$

θ_I and θ_I' are the molar feed ratios of inert I in the reaction side and permeation side to methane at the inlet of the reaction side. λ_i is the dimensionless permeability of species i through the reactor wall, which is a measure of the permeability of species i relative to the initial methane flowrate.

$$\lambda_i = \frac{A_i C_T \lambda_i'}{\Delta_i F_{CH_4}^o} \quad (7.87)$$

where A_i and Δ_i are the area and thickness of the reactor wall for the permeation of species i . C_T is the total concentration and τ is the ratio W/F , based on the methane flowrate at the inlet

$$\tau = W_c / F_{CH_4}^o \quad (7.88)$$

where W_c is the catalyst weight. We define a dimensionless contact time (or Damköhler number) by

$$Da = k_1 C_T^{1.90} W_c / F_{CH_4}^o \quad (7.89)$$

The system equations are integrated by the fourth order Runge-Kutta method with adaptive stepsize control. The overall feed ratios of oxygen to methane for all types of reactors are optimized so that the C_2 yield achieved at the outlet of the reactor is maximized. Although it has been suggested that the selectivity is the most important factor in practical applications of OCM, because unreacted methane can always be separated and recycled, the maximal C_2 yield (which is the methane conversion multiplied by C_2 selectivity) was chosen as the optimization criterion here due to the fact that searching for an optimal methane to oxygen ratio to maximize C_2 selectivity would always end up with a trivial solution: infinite methane to oxygen ratio and 100% C_2 selectivity. One of the possible alternative candidates for an optimization criterion is the sum of the C_2 yield and C_2 selectivity, for which a value of 100% is considered as the threshold value to make the OCM process commercially feasible. In the determination of the optimal overall feed ratio for the co-feed reactor, the uniformly distributed multiple stage-feed reactor, and the membrane-feed reactor, the Golden Section search method was used. The Hooke-Jeeves method [49] was employed to find the optimal feed distribution functions for optimally distributed multiple stage-feed and membrane-feed reactors, as more than one variable was required to be optimized.

7.2.3 Results

Figure 7-14 shows the axial profiles of methane to oxygen ratio and methane conversion for reactors with different numbers of oxygen feed points at 750°C, 1 atm, and contact time (catalyst weight to initial methane flowrate) of 50 g sec/mmol. For all of the reactors considered here, the feed positions of oxygen are evenly spaced with the first feed at the inlet, and the amount of oxygen introduced is equally distributed among the feed points. For example, if we feed oxygen at three feed points ($N=3$), they are the inlet, one-third, and

two thirds of the reactor. As can be seen from Figure 7-14, the methane to oxygen ratio increases as oxygen is being consumed until one-third of the reactor length, where the second feed of oxygen is introduced and a drop in the methane to oxygen ratio appears, then it increases again until the third feed is introduced. As the number of feed points N increases (say to one million), it essentially approaches a membrane-feed reactor. If we compare the co-feed reactor and the membrane-feed reactor, the methane to oxygen ratio is higher for the membrane reactor in the early part of the reactor. Although the co-feed reactor has a higher methane to oxygen ratio in the latter part of the reactor, it does not help much because, as indicated by the methane conversion profile, the reactions in the co-feed reactor are almost finished in the region close to the inlet. Therefore, since the methane conversion is more spread out over the reactor length in a membrane reactor, it is easier to remove the heat generated by the highly exothermic OCM reactions to control the hotspot temperature in a membrane reactor than in a co-feed reactor. Another advantage of using a membrane-feed reactor is that higher methane conversion could be achieved than in a co-feed reactor, where the highest oxygen inlet concentration is limited by the explosion limit. Because of the higher ratio of methane to oxygen, the membrane reactor gives the highest selectivity and yield as shown in Figure 7-15.

Figure 7-14a. Axial profiles of methane to oxygen ratio

Figure 7-14b. Axial profiles of methane conversion

Figure 7-15a. Axial profiles of C_2 selectivity.

Figure 7-15b. Axial profiles of C_2 yield

Figure 7-16 shows the maximum C_2 yield at the reactor outlet as a function of contact time (W/F_{CH_4}) for co-feed reactor, membrane-feed reactor, and multiple stage-feed reactor with the numbers of feed points $N=2, 3, 5, 10, 20, 50, 100$, and 200 at 750°C , and 1 atm with no dilution gas addition and no product removal through the reactor wall. Since the reaction orders in oxygen for C_2 formation are lower than those for CO_2 formation, the distributed feed of oxygen causes a relatively low oxygen concentration in the reactor and an increase in the number of feed points will help to decrease the oxygen concentration. So, both C_2 selectivity and yield increase with the number of feed points and the membrane reactor, in which the number of feed points is infinity, gives the highest selectivity and yield for the same contact time. In the low contact time region the co-feed reactor offers slightly higher yield and

Figure 7.16. Effect of contact time on maximum C_2 yield for reactors with different numbers of oxygen feed points

selectivity than the distributed feed reactors. As the contact time increases, the yield is more and more determined by selectivity. For the co-feed reactor, as shown in Figure 7-14, the reaction takes place in the reactor section close to the inlet, where the oxygen concentrations (thus the selectivity) are higher than those in distributed oxygen feed reactors. In the case of distributed oxygen feed reactors, longer contact time means lower local oxygen concentration or higher selectivity. As a result, as the contact time increases the C_2 yields of distributed reactors continue to increase while the C_2 yield of the co-feed reactor levels off. Thus, as can be seen from Figure 7-16, for contact times longer than a certain value (which is ca. 400 gsec/mol in this case), the maximum C_2 yield of membrane-feed reactor is higher than that of a co-feed reactor operated at the same contact time, temperature and pressure. The improvement of C_2 yield by using reactors with a distributed feed of oxygen becomes greater as the contact time and/or the number of feed points increase. These are consistent with the general analysis results [48, 50]. It can be concluded that the contact time needs to be high enough for the distributed reactors to make a significant improvement in the C_2 yield obtained by the co-feed reactor. A similar statement was made by Reyes et al. [37], although they did not optimize methane to oxygen ratio in their comparison study. In principle, 100 % C_2 yield could be realized when both the stage number and contact time approach infinity. Another advantage of using a distributed oxygen feed reactor is that it leads to a higher ethylene to ethane ratio as shown in Figure 7-16, where the membrane-feed reactor gives a ethylene to ethane ratio of 18, while the co-feed reactor gives 2 at high contact time. This is because of the fact that lower oxygen concentration in the membrane-feed reactor suppresses the ethylene oxidation reaction, which has a higher oxygen reaction order than the ethane and ethylene formation reactions.

It should be noted that all the results shown in Figure 7-16 were obtained at optimal feed ratios of oxygen to methane. Figure 7-17 shows the C_2 yields of both co-feed and membrane-feed reactors, operated at 750°C and 1 atm, comparing the optimal feed ratio to

Figure 7-17. Comparison of maximum C_2 yield in co-feed and membrane-feed reactors with optimal and fixed feed ratio

an oxygen to methane feed ratio of 0.5. The C_2 yield achieved at optimal conditions is about 4~5% higher than that at feed ratio of 0.5, and the optimal oxygen to methane ratio depends on contact time and is very different for the two configurations. For contact time less than ca. 3000 $\text{gm sec}/\text{mol}$, the optimal oxygen to methane ratios are high enough to be within the explosion region of methane-oxygen mixtures. Since methane and oxygen are fed separately in a membrane-feed reactor, the reactor can be operated at high overall oxygen to methane ratio without explosion, provided that the membrane integrity and seals are not compromised.

It is interesting to compare the oxygen permeation rates implied by the optimization results with those that have been experimentally measured. The parameter that is optimized in the model equations is the feed ratio or feed distribution function. The oxygen permeance is not explicit in the model equations, and the oxygen permeances required also depend on

the reactor geometry and operation parameters. Let us take a lab-scale porous Vycor glass membrane reactor [34] as an example. The oxygen flowrate through the membrane is about 7.5 ml/min at a pressure difference across the membrane of 400 kPa for a 10 cm long membrane tube. For a typical methane flow rate of 5-40 ml/min, this oxygen flowrate is equivalent to a O_2/CH_4 ratio of 0.2-1.5, which is similar to that required in the present modeling study. The feed ratio can be adjusted by changing the pressure difference across the membrane, the reactor length, the membrane thickness and void fraction to allow the membrane reactor to operate at its optimal feed ratio. In the case of a dense membrane reactor, the permeability of an oxygen permeable dense membrane developed in our lab at 800 °C and 1 atm is 2-4 cc/min cm^2 , which is equivalent to an oxygen flow rate of 40-80 ml/min for a 7 mm ID and 10 cm long membrane tube. This is even higher than the oxygen flow rate of the porous Vycor membrane reactor mentioned above.

A comparison of reactor performance between reactors with equally distributed and optimally distributed feed of oxygen is shown in Figure 7-18, in which the axial distributions of oxygen of different types of reactors as well as their yields and selectivities are given at $T=800^\circ C$, $P=1$ atm, $\tau=131$ g sec/mmol without dilution gas and product removal. For reactors with discrete oxygen feed points, the oxygen distribution is given by the molar ratio of the oxygen introduced at a particular feed point to the methane initially fed to the reactor; while for the reactors with continuous oxygen feed, the distribution is given by the oxygen distribution function, and the integration of this function from $t=0$ to t would be the molar ratio of the oxygen introduced from $t=0$ to t to the methane fed to the reactor inlet. The C_2 yield obtained in a co-feed reactor where oxygen is fed at the inlet (solid diamond in Figure 7-18) is 21.8%. Using an equally spaced and equally distributed multiple stage-feed reactor (solid circles), the C_2 yields become 27.04%, 34.70%, and 40.65% as the number of feed points increases from 2 to 5, to 10. The highest C_2 yield for an equally-distributed oxygen

Figure 7-18. Axial distributions of oxygen and C_2 yields and selectivities

feed (51.08%) is achieved by a membrane-feed reactor (solid line), which is equivalent to an equally distributed multiple stage-feed reactor with an infinite number of feed points. If an optimally distributed membrane reactor (dashed line) is used, instead of a uniformly distributed one, the improvement in the C_2 yield is not very significant. In this particular case, the C_2 yield is increased by only 0.2%. The same thing is true for multiple stage feed reactors with the same number of feed points. As an example, for 5 feed points, the yields obtained by an equally spaced and equally distributed feed reactor (solid circle), equally spaced and optimally distributed reactor (open triangle), and optimally spaced and optimally distributed reactor (open square) are 34.70%, 34.75%, and 34.85%. So, although the optimally distributed feed reactors result in higher maximum yield than evenly distributed feed reactors with the same number of feed points, the improvement in the C_2 yield is not as significant as that between reactors with different numbers of feed points.

Figure 7-19. Effect of temperature on the maximum C_2 yield and ethylene to ethane ratio.

The effects of temperature and pressure on the maximum C_2 yield and ethylene to ethane ratio are shown in Figure 7-19 and Figure 7-20. Because the activation energy of C_2H_6 formation used in this simulation is higher than that of CO_2 formation, the C_2 yield increases monotonically with temperature, which is consistent with the general experimental observations except at higher temperatures ($>800^{\circ}C$) when homogeneous reactions become predominant. This may result from the narrow range of temperature in which the kinetic data were evaluated, and the assumption of simple lumped kinetics, which might fail to describe the OCM process at higher temperatures. Due to the relatively low activation energy of ethane dehydrogenation to that of ethane formation, the ethylene to ethane ratio begins to decrease at higher temperatures.

Figure 7-20. Effect of pressure on the maximum C_2 yield and ethylene to ethane ratio

Increasing total pressure has two opposite effects on the yield. First, the dimensionless contact time (Da) is proportional to the total concentration and higher total pressure (or higher dimensionless contact time) results in higher C_2 yield. On the other hand, the increase in total pressure also increases the partial pressure of oxygen, which leads to lower C_2 selectivity according to the earlier discussion. At low pressures, the dimensionless contact time is short and the yield is determined by the conversion, so the yield increases with pressure. In the high pressure region, the selectivity becomes more important and further increase of pressure is detrimental to the C_2 yield. The effect of total pressure on the ethylene to ethane ratio follows the same trend to that on the C_2 yield except that the optimal total pressures are shifted to higher values.

Figure 7-21. Effect of dilution gas on the maximum C_2 yield

Since dilution gases have been used in most of the OCM experiments reported in the literature, it is necessary to investigate the effect of the addition of dilution gases on the reactor performance. From Figure 7-21 we see that dilution gas addition leads to higher C_2 yields, but longer contact time is required to achieve the same C_2 yield for any type of reactor considered here. For a reactor with a dilution ratio of 10 (initial feed ratio of inerts to methane), about 20-50 times longer contact time is required to achieve a similar level of C_2 yield to a reactor without dilution gas. Since a membrane reactor needs a longer contact time to show its advantage over a co-feed reactor, this means that much longer contact times would be required by a membrane reactor with dilution gas addition, compared to the contact times at which most of the co-feed packed-bed reactors have been operated.

Figure 7-22. Dependence of maximum C_2 yield on C_2 permeability in distributed oxygen-feed reactors with C_2 removal

The C_2 yield can be greatly improved if the wall of the reactor is selectively permeable to C_2 products. The improvement in C_2 yield by the removal of one or both of the desired products (ethane and ethylene) is illustrated in Figure 7-22. It is obvious that, for all the reactors with different types of oxygen feeding modes, an increase in C_2 product permeability results in higher maximum C_2 yield. For a membrane-feed reactor, for example, the highest C_2 yield that can be achieved by a reactor with a non-permeable wall to C_2 (on the left side of the graph) is about 19.3% under the particular conditions. However, a membrane-feed reactor with a C_2 -permeable wall could give a C_2 yield up to 29.6%. When the dimensionless permeabilities reach 1000, the yield begins to level off because nearly all the C_2 formed has been removed. This is in agreement with the result obtained by Bernstein and Lund [51] regarding the effect of permeability ratio of intermediate product to the reactant in a study of series-parallel reactions in membrane reactors. It also can be seen that desired product removal helps the membrane feed reactor more than the co-feed reactor.

It is interesting to notice that selective removal of ethylene is more effective than the removal of ethane in the low permeability region. This is due to the fact that, at low C_2 permeability, the C_2 concentration is higher, and both ethane dehydrogenation and ethylene oxidation are important. Selective removal of ethylene, which suppresses the ethylene oxidation reaction, results in higher C_2 yield than ethane removal. In the higher permeability region, where the C_2 concentration is low and the ethylene oxidation reaction becomes less dominant. So, the removal of ethane, which reduces the ethylene concentration and thus suppresses the ethylene oxidation, becomes more and more effective.

Using a C_2 product-removal membrane reactor will greatly reduce the contact time that would be required by reactors without C_2 removal. In practice, though, it is difficult to make a reactor wall that is only permeable to C_2 except using special interstage separation techniques for multiple reactor systems [44-45]. Figure 7-23 shows the effect of methane permeability on the maximum C_2 yield at a separation factor of C_2 to CO_2 and H_2O of 5 and

Figure 7-23. Effect of methane permeability on the maximum C_2 yield in distributed oxygen-feed reactors with product removal

compared with the non-permeable wall situation, at 750°C, 1 atm, and 10 g sec/mmol. For C_2 to CH_4 separation factors below 200 (corresponding to dimensionless permeability of methane equal to 5, in Figure 7-23), the yield of the permeable wall reactor gives a lower yield than the non-permeable one due to the loss of methane to the permeation side, and the membrane-feed reactor is worse than a co-feed reactor. This suggests that a low methane permeability is critical for product-removal reactors to be effective.

7.2.4 Summary

To make oxidative coupling a commercially feasible process, the use of cross-flow reactors can be an effective way to achieve higher C_2 selectivity and yield. Using a distributed oxygen-feed reactor, a reactor that selectively removes C_2 products, or a two-membrane reactor with both oxygen feed and product removal could greatly improve the reactor performance compared to the conventional co-feed reactor. Reactor with distributed feed of oxygen can be operated at high oxygen to methane ratio without explosion. For multiple stage oxygen-feed reactors with the same numbers of feed points, evenly and optimally distributed oxygen-feed reactors almost give the same maximum C_2 yield. Keeping a high separation factor of C_2 to methane is crucial to the product-removal membrane reactor to achieve higher C_2 yield. Also, reasonable comparison of reactor performances between different types of reactor should be made under their optimal conditions.

Chapter 8. Conclusions

Extensive experimental efforts have been made to investigate methane oxidative coupling using inorganic membrane reactors. Porous and dense ceramic membrane reactors were developed and methane-coupling experiments were conducted using different reactor configurations and operating conditions, and using different catalysts. The experimental results clearly demonstrated the beneficial effect of the distributed feed of oxygen along the reactor length for the methane oxidative coupling reactions. Significant achievements have been made in all aspects of the project such as material synthesis, membrane preparation and modification and module design, as well as in theoretical modeling.

A membrane reactor with a thermally treated porous Vycor glass membrane tube was fabricated for the study of methane oxidative coupling. Experimental results showed that, under equivalent conditions, C_2 selectivities were 10% higher in the membrane reactor, compared to the conventional co-feed non-porous reactors, in the temperature range of 650°C to 850°C. Studies involving variation of methane to oxygen ratios showed that both the methane conversions and C_2 selectivities were highest at a methane to oxygen ratio of 2.0. Experiments run at conditions where the oxygen conversion was less than 100% resulted in lowered C_2 selectivity and higher methane conversions because of oxygen availability. Experiments involving metering of methane flow from the high-pressure shell side into a mixture of oxygen and helium on the catalyst packed tube side showed that improved hydrocarbon selectivity was overshadowed by a lowered methane conversion. These results indicate that metering the oxygen flow through porous membrane reactors is beneficial for the methane coupling reaction when most of the oxygen supplied to the catalyst bed is used up before exiting the reactor. Modeling studies focused on fitting the experimental results obtained in the VYCOR membrane reactor with a simplified kinetic model. The parameters for the fit were obtained by using

the experimentally obtained values of methane conversions and C_2 selectivities and yields from fixed bed reactor experiments. The trends in experimental data on methane conversions, and C_2 selectivities and yields agreed reasonably well with the predicted trends of the model.

A porous gamma alumina membrane reactor was employed to study methane oxidative coupling with Mn-W-Na/SiO₂ catalyst packed inside the membrane tube. The gamma-alumina membrane tube was thermally stabilized by treating the membrane tube with La(NO₃)₃ aqueous solution and calcining at 900°C. C_2 yields up to 27.5% were achieved, which is the highest C_2 yield reported in the literature for the methane oxidative coupling reaction in a membrane reactor. This yield is close to that required for successful commercialization of methane oxidative coupling.

Although the porous membrane reactor showed lower methane conversion than a conventional co-feed fixed bed reactor at the same reaction conditions, it gave higher C_2 selectivity and C_2 yield at similar methane conversions. By varying the helium flow rate and keeping the temperature, methane flow rate, and oxygen flow rate constant, the membrane reactor gave 10% higher C_2 yield and 30% higher C_2 selectivity than the co-feed reactor operated at the same methane conversion. At similar C_2 yield and C_2 selectivity, the methane conversion of the membrane reactor was 15% lower than that of the co-feed reactor. By varying the oxygen flow rate and keeping the temperature, methane flow rate, and helium flow rate constant, at the same methane conversion, the membrane reactor gave about 3% higher C_2 yield and C_2 selectivity than the co-feed reactor. Higher helium flow rates gave higher C_2 selectivity and yield, whereas changing methane flow rate did not significantly affect the reactor performance.

The oxidative coupling of methane was also studied with various oxygen-permeable dense membrane reactors. The first dense membrane was a non-perovskite material (SrFeCo_{0.5}O_{3-δ}) with both oxygen ion and electron conductivities. The flux of oxygen through the dense membrane tube was measured with air fed in the shell side of

the reactor module and helium in the membrane tube. The oxygen flux was about 0.04 cc(STP)/min cm² at 950°C under non-reaction conditions. The oxygen flux increased with an increase in either helium sweep flow rate, the air flowrate, or temperature. When methane was fed into the tube side and air into the shell side, only CO₂ with no detectable C₂ hydrocarbons was observed in these experiments at temperatures of 770 to 910°C, which suggested that the dense membrane material was a total oxidation catalyst. When reactions took place in the membrane tube, the oxygen flux was found to be about four times higher than that observed under non-reaction conditions. In order to reduce the total oxidation of hydrocarbons catalyzed by the dense membrane material, a perovskite oxide material (BaCe_{0.6}Sm_{0.4}O₃) was coated on the inner wall of the dense membrane tube. This material was known from literature to be active for OCM. La/MgO catalyst, which was prepared by a precipitation method, was packed inside the dense membrane tube. Methane mixed with helium flowed in the tube side, while air was fed to the shell side. The oxygen flux values under non-reaction condition were only about 30% of those obtained with an uncoated dense membrane tube. Compared to the co-feed reactor configuration (i.e. co-feeding oxygen and methane to the tube side of the same membrane reactor setup) at the same methane conversion level, the membrane reactor gave higher C₂ selectivity in the low methane conversion region. Although the reactor performance was improved by coating the tube with BaCe_{0.6}Sm_{0.4}O₃, the C₂ yield was still less than that observed in the conventional packed-bed reactor due to the interaction of the reactant mixture and C₂ products with the dense membrane surface that was not covered by the coating material. Therefore, a second dense membrane tube was prepared using a material with both the oxygen conducting property and methane coupling activity.

A powder of a perovskite material (BaCe_{0.8}Gd_{0.2}O₃) with both electronic and ionic conductivity was synthesized by the ethylene glycol method. A dense membrane tube was fabricated from this material using a plastic extrusion technique. The oxygen permeance of the dense membrane tube was measured as a functions of temperature and of oxygen partial pressure on the feed side. In the temperature range of 688°C to 955°C, the dependence of oxygen flux on the temperature obeyed the Arrhenius law. The oxygen

flux increased proportionally with the natural logarithm of the oxygen partial pressure in the feed side, as predicted by theory. Experimental results in the absence of additional catalyst, showed that this material had fairly good catalytic activity towards the methane coupling reactions. Yields of C_2 hydrocarbons of up to 16% were achieved in the $BaCe_{0.8}Gd_{0.2}O_3$ dense membrane reactor. The dense membrane remained stable after one month's continuous running. Although the improvement in C_2 hydrocarbon yield was not significant compared to results from the same dense membrane reactor operated in co-feed mode, the use of the oxygen-permeable dense membrane reactor offers the advantage of using air as the oxygen source without costly down-stream separation of nitrogen.

Catalytic results for the high temperature oxidative coupling of methane in cross flow radial membrane reactors indicated an interesting new direction for membrane design. By exploring the reactor performance in membranes of pore diameters of 2.0 μm , 0.2 μm , and 0.02 μm , the effect of the flow regime on the methane coupling activity could be investigated. In these studies, the active Sm_2O_3 catalyst was deposited on the pore walls. The smaller pore (0.02 μm) diameter membrane reactor showed much higher hydrocarbon selectivity than the other two membrane reactors when the catalyst was evenly deposited on the pore walls. Theoretical calculations indicate the flow regime in this 0.02 μm membrane reactor to be in the Knudsen region and was confirmed by diffusion studies, in contrast to the higher pore diameter membrane reactors where the flow is predominantly viscous flow. These results are important for OCM and other selective hydrocarbon reactions. Under similar flow conditions, the 0.02 μm radial reactor afforded substantially higher C_2 yields than packed reactors. Since this configuration ensures that all of the catalytic surface interacts with reactants, significantly higher conversions were obtained. Markedly higher selectivities resulted from the radial bed operating in Knudsen flow regime which is a configuration which reduces the possibility of C_2 products reacting with adsorbed metal oxides, which is known to lead to non-selective products.

Oxygen conducting perovskites were synthesized using conventional as well as cavitation techniques and were characterized by XRD, TGA and DSC. $\text{Sr}_{0.8}\text{La}_{0.2}\text{FeO}_3$, an oxygen conducting perovskite that was synthesized by hydrodynamic cavitation showed interesting DSC and TGA spectra that indicated a change in the crystal structure at relatively moderate temperatures of 150°C and 350°C . Perovskites composed of lanthanum, strontium and iron, which form good oxygen conductors, showed very poor methane coupling activity in comparison to the commonly used methane coupling catalyst, samarium oxide. Hence, a dense membrane reactor that employs this material for metering oxygen flow for methane coupling might inherently cause very low hydrocarbon selectivities. On the other hand, perovskites of the strontium-cerium-ytterbium series showed moderate activity for methane coupling, which lay between that of samarium oxide and the La-Sr-Fe oxides. Since these Sr-Ce-Yb-oxides also show moderate oxygen conduction properties, they might be better choices as potential candidates for dense membranes in membrane reactors.

Experiments aimed at modifying the porous alumina included stabilization of gamma alumina and pore filling of alpha alumina supports. The lanthanum modified alumina exhibited lower permeance as compared to the unmodified alumina, indicating that either a partial pore blockage or a change in morphology had occurred in the alumina substrate. A high-pressure technique based on *cavitation* effects in fluids was used to synthesize nanometer size LaAlO_3 particles which were deposited inside the 1.2 micron pores of the alpha alumina substrate. A lowering of gas permeance was achieved, wherein gas permeance decreased with increasing number of pore fillings. It is important to note that the permeabilities after heating at 900°C were similar to a fresh 40 Å alumina membrane. Thus, this is a new approach for the synthesis of porous membranes, stable at higher temperatures.

A mathematical model was proposed for the simulation of distributed feed reactors with six types of feed policies. All of the six types of distributed feed reactors were analyzed for general series-parallel reaction systems and their optimal feed

distributions were determined by maximizing the desired product yield at the outlet of the reactor. The performances of reactors with different types of feed policies were compared based on the same dimensionless residence time. For reaction systems with a lower order in the distributed reactant for the desired reaction than that for undesired reactions, higher yield and selectivity of the desired product could be achieved by reactors with staged feed than by conventional co-feed reactor, operated at the same conditions. Staged feed reactors required sufficiently high residence time to significantly improve the desired product yields and selectivities over those obtained by a plug flow reactor. In addition to the kinetic order and residence time requirements, the rate constants of the reactions involved have to fall within certain ranges for the distributed feed reactor to obtain higher maximum yield than one-stage co-feed reactors. Unevenly distributed feed reactors always give higher maximum product yields than evenly distributed reactors with the same number of feed points. However the improvement of yields is not as great as that between the plug flow reactor and evenly distributed reactors. On the other hand, for reaction systems with higher order with respect to the distributed reactant in the desired reaction than the undesired reactions, co-feed reactors always give higher yield than staged feed reactors.

A staged-feed reactor model with distributed feed of oxygen and product removal for the oxidative coupling of methane was developed, and comparison studies were carried out to analyze the different performance of reactors with different configurations in terms of contact time, temperature, pressure, dilution ratio, and permeability. For each of the reactor configurations considered, the overall methane to oxygen feed ratio was optimized such that the C_2 yield at the reactor outlet was maximized. Modeling results showed that distributed feed oxygen could give rise to much higher C_2 yields than the co-feed reactor, as long as the ratio of catalyst loading to initial methane flowrate was sufficiently high. Although reactors with optimally distributed oxygen feed gave higher C_2 yields than evenly distributed ones, the improvement was not significant. In the case of a two-membrane reactor, where one membrane is used for oxygen feed and the other for C_2 product removal, higher C_2 yields could be obtained than in a single membrane

reactor with distributed oxygen feed. However, if the membrane for C_2 product removal is also permeable to other species as well as to C_2 products, low permeability of methane is critical to the achievement of high C_2 yield.

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APPENDIX A

A1. Thermodynamic Calculations of Maximum Theoretical Hydrocarbon Yields

The products observed in the high temperature catalytic activation of methane are mainly CO_2 , H_2 , C_2H_6 , C_2H_4 , CO , and H_2O . The maximum C_2 yields would be achieved if there were no formation of CO_x (that is the C_2 hydrocarbon selectivity could go up to 100%). Since almost all the methane coupling experiments are carried out with excess of methane, we assume that there is no oxygen left in the product stream. From the phase rule, the degree of freedom (f) for any system at equilibrium at constant temperature and pressure is

$$f = c - p - s \quad (2.1.1-1)$$

Here the number of component c is equal to 5 (CH_4 , C_2H_6 , C_2H_4 , H_2 , and H_2O), the number of phase p is 1 (gas phase), and the number of additional constraints s is 2 ($\text{N}_{\text{H}_2\text{O}} = 2\text{N}_{\text{O}_2}^0$ and $4\text{N}_{\text{CH}_4} + 6\text{N}_{\text{C}_2\text{H}_4} + 4\text{N}_{\text{C}_2\text{H}_6} = 4\text{N}_{\text{CH}_4}^0$). Therefore the degree of freedom f is 2. That is to say, to get the theoretically highest C_2 yields two independent chemical reactions are sufficient for calculation of product distribution. If one chooses the following 2 reactions:

Starting with 1 mole of methane, a mole of oxygen and b mole of inert, the equilibrium composition will be

	CH ₄	C ₂ H ₆	C ₂ H ₄	H ₂	H ₂ O	Inert
Number of moles	1-2x-2y	x	y	x+2y-2a	2a	b

Total number of moles, $N_i = 1 + b + y$

where x and y are the extents of reactions 2.1.2-2 and 2.1.1-3 respectively at equilibrium.

For the system at equilibrium at 1 atm

$$K_1 = x(x+2y-2a)/(1-2x-2y)^2 \quad (2.1.1-4)$$

$$K_2 = y(x+2y-2a)^2/[(1-2x-2y)^2(1+b+y)] \quad (2.1.1-5)$$

where K_1 and K_2 are the equilibrium constants of reaction (2) and (3) and

$$K_1 = \exp\{-(G_f^0, \text{C}_2\text{H}_6 + G_f^0, \text{H}_2) - (2G_f^0, \text{CH}_4)]/(RT)\} \quad (2.1.1-6)$$

$$K_2 = \exp\{-(G_f^0, \text{C}_2\text{H}_4 + 2G_f^0, \text{H}_2) - (2G_f^0, \text{CH}_4)]/(RT)\} \quad (2.1.1-7)$$

The Gibbs free energies of formation as a function of temperature are correlated by the following polynomials

$$G^0_{f, CH_4} = -73.184 + 6.5276 \times 10^{-2} T + 3.8075 \times 10^{-5} T^2 - 1.0762 \times 10^{-8} T^3 \quad (2.1.1-8)$$

$$G^0_{f, C_2H_6} = -82.424 + 15.344 \times 10^{-2} T + 5.5360 \times 10^{-5} T^2 - 1.5729 \times 10^{-8} T^3 \quad (2.1.1-9)$$

$$G^0_{f, C_2H_4} = 53.507 + 3.9813 \times 10^{-2} T + 3.5335 \times 10^{-5} T^2 - 0.96517 \times 10^{-8} T^3 \quad (2.1.1-10)$$

$$G^0_{f, H_2} = 0 \quad (2.1.1-11)$$

The solutions of equations (4) and (5) are

$$y_1 = (-b_{21} + 21^{1/2})/2 \quad (2.1.1-12)$$

$$y_2 = (-b_{21} - 21^{1/2})/2 \quad (2.1.1-13)$$

$$y_3 = (-b_{22} + 22^{1/2})/2 \quad (2.1.1-14)$$

$$y_4 = (-b_{22} - 22^{1/2})/2 \quad (2.1.1-15)$$

$$x_i = 2y_i(y_i - a)/[(r-1)y_i + r(1+b)] \quad I=1,2,3,4 \quad (2.1.1-16)$$

where,

$$21 = b_{21}^2 - 4c_{21} \quad (2.1.1-17)$$

$$22 = b_{22}^2 - 4c_{22} \quad (2.1.1-18)$$

$$b_{21} = (a_4 + 2^{1/2})/2 \quad (2.1.1-19)$$

$$b_{22} = (a_4 - 2^{1/2})/2 \quad (2.1.1-20)$$

$$c_{21} = z_0' + (a_4 z_0' - c_4)/2^{1/2} \quad (2.1.1-21)$$

$$c_{22} = z_0' - (a_4 z_0' - c_4)/2^{1/2} \quad (2.1.1-22)$$

$$2 = 8z_0' + a_4^2 - 4b_4 \quad (2.1.1-23)$$

$$z_0' = z_0 - b_3/3 \quad (2.1.1-24)$$

$$z_0 = 2s_3 \cos(\theta/3) \quad \text{if } \theta < 0 \quad (2.1.1-25)$$

$$z_0 = 2(-q_3/2)^{1/3} \quad \text{if } \theta = 0 \quad (2.1.1-26)$$

$$z_0 = (-q_3/2 + 3^{1/2})^{1/3} + (-q_3/2 - 3^{1/2})^{1/3} \quad \text{if } \theta > 0 \quad (2.1.1-27)$$

$$\theta = q_3^{4/4 + p_3^3/27} \quad (2.1.1-28)$$

$$s_3 = r_3^{1/3} \quad (2.1.1-29)$$

$$= \arccos(-q_3/2r_3) \quad (2.1.1-30)$$

$$r_3 = (-p_3^3/27)^{1/2} \quad (2.1.1-31)$$

$$p_3 = (3c_3^2 - b_3^2)/3 \quad (2.1.1-32)$$

$$q_3 = (2b_3^3 - 9b_3c_3 + 27d_3)/27 \quad (2.1.1-33)$$

$$b_3 = -b_4/2 \quad (2.1.1-34)$$

$$c_3 = (a_4c_4 - 4d_4)/4 \quad (2.1.1-35)$$

$$d_3 = [d_4(4b_4 - a_4^2) - c_4^2]/8 \quad (2.1.1-36)$$

$$a_4 = [-2ap^2 + 2p(u+q-a) + 4v(2q-1)]/(p^2 + 2p + 4v) \quad (2.1.1-37)$$

$$b_4 = [a^2p^2 + 2p(uq - ua - qa) + v(4q^2 - 8q + 1)]/(p^2 + 2p + 4v) \quad (2.1.1-38)$$

$$c_4 = [-2puqa - 2vq(2q-1)]/(p^2 + 2p + 4v) \quad (2.1.1-39)$$

$$d_4 = vq^2/(p^2 + 2p + 4v) \quad (2.1.1-40)$$

$$u = (a - 2K_1)/(4K_1 - 1) \quad (2.1.1-41)$$

$$v = K_1/(4K_1 - 1) \quad (2.1.1-42)$$

$$p = 2/(r-1) \quad (2.1.1-43)$$

$$q = r(1+b)/(r-1) \quad (2.1.1-44)$$

$$r = K_2/K_1 \quad (2.1.1-45)$$

Of the 4 sets of solutions (x_1, y_1) , (x_2, y_2) , (x_3, y_3) , and (x_4, y_4) , only the set of solution that satisfies the conditions of $0 \leq x_i \leq 1$ and $0 \leq y_i \leq 1$ has physical meaning. And the maximum yield Y^* is

$$Y^* = 2(x+y) \quad (2.1.1-46)$$

APPENDIX B

B1. SYNTHESIS AND CHARACTERIZATION OF OXYGEN CONDUCTING PEROVSKITES

B1.1 Perovskite Synthesis Techniques.

The oxygen semi-permeability in perovskite type oxides ($\text{La}_{1-x}\text{A}_x\text{MO}_{3-\delta}$) is correlated with the mixed conductivity of the perovskites. This mixed conductivity arises from the following : (1) the mixed valence state of the 3d transition metals, M, which results in high electron conductivity; (2) the large oxygen non-stoichiometry, which is related to the high diffusivity of the oxide ions; (3) the composition of the complex oxide. Teraoka *et al.* [1], showed the effect of the cation substitution as an increase of the rate of oxygen permeation through $\text{La}_{0.6}\text{A}_{0.4}\text{Co}_{0.8}\text{B}_{0.2}\text{O}_3$ at fixed temperature as the 'A' cation is replaced successively by $\text{Na} < \text{Sr} < \text{Ca} < \text{Ba}$, and the 'B' cation by $\text{Mn} < \text{Cr} < \text{Fe} < \text{Co} < \text{Ni} < \text{Cu}$; and finally, (4) the stoichiometry and the crystallographic structure. which along with the composition, surface structure and morphology of the final product is determined by the preparation procedure.

The perovskite-type ferrites $\text{La}_{(1-x)}\text{Sr}_x\text{FeO}_{3-\delta}$ have been extensively studied. The choice of the degree of Sr substitution is based on the consideration of a good compromise between the electronic and ionic conductivities. Kim *et al.* [2] have studied the dependency of Sr composition on the electrical conductivity, oxygen self-diffusion coefficient D, and oxygen vacancy concentration. Their study concluded that both electric conductivity and oxygen self- diffusion are maximized in perovskite-type oxide $\text{La}_{0.4}\text{Sr}_{0.6}\text{FeO}_{3-\delta}$ as seen in Figure 1. (i.e. $x=0.6$ in the above formula). We have synthesized the series of these Sr-substituted perovskite-type ferrites, and the XRD

spectra of these compounds are presented in Figure 2. It can be seen that the perovskite structure ($x=0$) is retained fairly well until the Sr concentration reaches 0.6 ($x=0.6$). Based on these results the objective of the membrane modification is to observe the effect of different membrane modification factors on the transport mechanisms, by studying the permeation properties.

Two main synthesis routes were generally followed for preparing these perovskite-type oxides. A mixed solid oxide process (which consists of the decomposition of precursor compounds containing the desired metal ion in air or oxygen) and a solution process (evaporation and decomposition allow intimate mixing of the metal ions in the precursors and synthesis at low temperature results in high surface areas). In preparing the perovskite for depositing in the porous membranes, we have used the following kinds of solution methods :

- the co-precipitation method : A precipitating agent is added to a solution containing the precursor compounds. The homogeneity and the degree of atomic mixing of the metal ions in the precipitates depend on the solubility products of the compounds involved.

- the sol-gel method : An amorphous gel is first synthesized from a solution of the corresponding metal nitrates mixed with a gelling pre-cursor. Ethylene glycol has been used as the pre-cursor in the sol-gel technique employed in this research. The deposited gel is then dried and calcined to the oxide form. This technique will be referred to hereafter as the Ethylene Glycol Technique.

B1.1.1 Ethylene Glycol Technique

After trying different methods of preparation, we chose the ethylene glycol technique which allowed the synthesis of pure perovskite at low temperatures. Perovskite synthesis using the ethylene glycol technique involves the following steps:

- Precursor solution of the corresponding nitrates of La, Sr, Co and Fe are mixed in an excess of ethylene glycol.
- The nitrate solution is gradually heated to 200°C on a hot plate, with continuous stirring to evaporate excess ethylene glycol and form a gel.
- The gel is calcined for 24 - 48 hours in the temperature range 800°C - 1000°C to form the perovskite.
- Perovskite structure is seen to evolve after 700°C, with the phase purity increasing with the calcination temperature.

The precursor solution of $\text{La}_{0.4}\text{Sr}_{0.6}\text{FeO}_{3-\delta}$ was prepared by dissolving the corresponding metal nitrates in ethylene glycol. In order to obtain the variations in Sr content in the perovskite-type oxides, the Sr concentrations in the solutions were varied relative to the formula equivalent, $\text{La}_{0.4}\text{Sr}_{0.6}\text{FeO}_{3-\delta}$ (0.1, 0.4, 0.6, 0.8 mol/l, see Table 2 below). X-Ray Diffraction spectra in Figure 2 show the crystallographic structure of $\text{La}_x\text{Sr}_{(1-x)}\text{FeO}_3$, verifying that perovskite structure is obtained.

Table B1. Starting compositions of precursors used for preparing Sr substituted perovskite-type oxides

Formula	Amount of Precursor (gms [no. of moles])			Sample ID
	Lanthanum nitrate $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ M.W. = 433.02	Strontium nitrate $\text{Sr}(\text{NO}_3)_2$ M.W. = 211.63	Iron nitrate $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ M.W. = 404.02	After calcination
LaFeO_3	4.3302[0.01]	-	4.0402[0.01]	AB102a
LaFeO_3	3.4642[0.008]	0.4233[0.002]	4.0402[0.01]	AB102c
$\text{La}_{0.2}\text{Sr}_{0.8}\text{FeO}_3$	2.5981[0.006]	1.2698[0.004]	4.0402[0.01]	AB102d

$\text{La}_{0.4}\text{Sr}_{0.6}\text{FeO}_3$	1.7321[0.004]	1.2698[0.006]	4.0402[0.01]	AB102b
$\text{La}_{0.2}\text{Sr}_{0.8}\text{FeO}_3$	0.8661[0.002]	1.6931[0.008]	4.0402[0.01]	AB111d
SrFeO_3	-	2.1163[0.01]	4.0402[0.01]	AB111b

B1.1.2 Membrane Synthesis Procedure

Incipient wetness was used for the perovskite-type oxide impregnation into porous membrane supports. This technique allowed the use of either an aqueous or a non-aqueous solvent. The technique consisted of pouring the metal precursors solution into the tube and the depositing the solute directly on to the support. The main parameters that were used to control the quality and amount of the deposit were the temperature, pressure, solution concentration; configuration of the apparatus and the contact time. Unless otherwise mentioned, the impregnation was made at room temperature and atmospheric pressure. The membrane-support tube was positioned vertically the tube was flipped over (turned upside down) after half of the contact time. The contact time was kept constant at ten minutes for most of the prepared membranes. The excess liquid was then decanted, and the tube was warmed in an electrical oven at 150°C to evaporate the solvent and to obtain an amorphous gel. The tube was then calcined first for 2 hours at 200°C to evaporate any residual solvent, and finally at 600°C for 20 hours to form the oxide. The temperature was raised stepwise, and maintained for two hours for every 100°C rise, between 200°C and 600°C in order to avoid extreme changes in temperatures which can damage the membrane. Cool-down was at the same rate, allowing a stress-relaxation step at 100°C overnight to release the stresses created during the calcination.

B2. Membrane-supports

The untreated ceramic membrane-supports used in our study were made of either alumina or zirconia, and were essentially meso-porous and tubular. Two types of alumina membranes were used as supports : an α -alumina membrane consisting of three layers with mean pore diameters of 2000, 8000, and 125000 Angstroms, and a gamma alumina membrane which contains a thin, 50 Angstrom pore diameter, γ -alumina layer on top of the smallest pore size α -alumina membrane (see Table B2 below). The zirconia membranes that were used had three pore sizes in the top thin layer : 200, 500, 1000 Angstroms.

Table B2. Structure of alumina membranes

LAYER	THICK (μm)	MATERIAL	PORE SIZE ($\text{\AA}$)	POROSITY (%)
1	3-5	γ -ALUMINA	50	50
2	30	α -ALUMINA	2000	35
3	50	α -ALUMINA	8000	40
4	1,500-2,000	α -ALUMINA	125,000	40-45

B3. PERMEATION MEASUREMENTS ON MODIFIED INORGANIC MEMBRANES.

B3.1 Experimental

The permeation apparatus was of shell-and-tube type. The tube side exit, as well as the shell side inlet are blocked. High purity gases fed into the tube side, permeate through the membrane and flow out of the shell. Gas flow rates were measured by a bubble flow meter for small flows (smaller than 1 liter/min), and a wet-testmeter for flows between 1 and 13 liter/min. The gas permeance was measured at room temperature.

The permeances of pure gases nitrogen, helium, Oxygen, and methane were measured at room temperature on both the original membranes and the membranes modified by perovskite deposition. In choosing a membrane for impregnation of oxides, several options were investigated. The commonly used ceramic membranes were alpha alumina membranes, gamma alumina membranes, zirconia membranes and porous VYCOR membranes. The choice of the membrane for impregnation was limited essentially by the stability of its oxide phase. For example, zirconia was limited by its tetragonal-monoclinic phase transformation, and gamma-alumina, by its allotropic transformation to alpha-alumina. The following describes our experiments with these inorganic membranes for achieving pore closure and efforts toward developing a dense membrane reactor for the oxidative coupling of methane.

B3.2 Alpha alumina membranes

Alpha alumina has very good high temperature stability up to 1000°C, but α -alumina membranes are not available commercially in pore sizes less than 2000 Angstroms. Systematic studies on variation of permeance across alpha alumina membranes of different pore sizes were performed. Permeance of various gases was investigated, as also the effect of change in these permeance values with increasing number of perovskite depositions and using different perovskite solution concentrations. Figure 4 shows the change in permeance of nitrogen gas through a 2000 Angstrom alpha alumina membrane with increasing number of perovskite depositions. The first four consecutive depositions cause a decrease in nitrogen permeance as shown in the first figure (A). Figure (B) shows the permeance change for nitrogen gas after the 4th, 5th, 6th, 7th and 8th deposition with perovskite solution concentrations of 0.4M and 0.6M. In this and other experiments with different gases, a leveling off of permeance value was observed after about 7 depositions (saturated permeance value $\cong 3 \times 10^{-6}$ mol/sec.m².Pa. in this case). Further depositions did not cause any more lowering of the permeance. Based on the premise that the higher concentrations of perovskite solutions might be too viscous to penetrate and fill the constricted pores, a set of experiments were devised where a few cycles of depositions are made at successively lower solution concentrations. Figure 5 shows the results obtained on a 2000 Angstrom pore size alpha alumina membrane where the concentrations of the perovskite solution were dropped from 0.8 M to 0.1 M and a total of 12 depositions have been made. The permeance of nitrogen gas seems to have saturated at 2.5×10^{-6} mol/sec.m².Pa. at the end of this experiment and this is about the lowest value of permeance obtainable so far in our experiments with alpha alumina membranes. Similar results were seen with helium gas where the permeance leveled off at $\cong 6 \times 10^{-6}$ mol/sec.m².Pa. as seen in Figure 6. In fact, the lowering of concentrations of the depositing solutions seems to be counterproductive after a few stages, since an increase in permeance is observed. The deposited perovskite was probably being washed away by the dilute perovskite solution. It is also possible that repeated calcination at high temperatures may change the membrane, developing cracks and thereby increasing the permeation rate.

A thermal treatment study has been carried out to observe the effect of high temperature calcinations between successive depositions. Table 3 below reports the loading (weight of perovskite deposited) after each deposition on alpha-alumina supports. The two membranes A6 and A7 are treated differently, A6 is calcined at 600°C after each deposition, while A7 is only subjected to a final calcination after the third deposition.

Table B3. Comparison of thermal treatments (successive vs. final) on perovskite loading of alumina membranes.

No. of Depositions	MEMBRANE A6		MEMBRANE A7	
	Weight of the Loading (gm)	Thermal treatments	Weight of the Loading(gm)	Thermal treatments
0	0	200°C then 600°C	0	200°C
1	0.1490	"	0.2490	200°C
2	0.3213	"	0.4860	200°C
3	0.4333	"	0.6597 0.4338	200°C , 600°C

From this study, we observed that the same loading weight for the oxide was obtained after three depositions and the 600°C calcination for both membranes, i.e. 0.433 gms. Furthermore, a comparable permeance was observed : about $5.2 \cdot 10^{-5}$ mol/s.m².Pa for nitrogen gas after the 600°C calcination. The permeance measurements carried out

on the alpha-alumina membrane A7 prior the final calcination step demonstrated lower values. Figure 7 shows the result for the A7 alumina membrane. The permeance to nitrogen which was $\cong 1.5 \times 10^{-5}$ mol/sec.m².Pa. after the third deposition jumped back to $\cong 5 \times 10^{-5}$ mol/sec.m².Pa. after a thermal treatment at 600°C.

Permeances of different gases through alumina membranes have also been measured in the course of this work. Four different gases were investigated for their permeance through the membranes: Nitrogen, Oxygen, Helium and Methane. Figure 8 shows the permeance values of different gases passed through an alpha alumina membrane that has undergone four depositions of a perovskite solution (solution concentration = 0.6 M).

B3.3 Gamma Alumina Membranes

Gamma alumina membranes are commercially available with a pore size of about 50 Angstroms and thickness of approximately 5 μ . Room temperature permeance of helium gas through these γ -alumina membranes was measured to be about 3.5×10^{-5} mol/sec.m².Pa. while the permeance for nitrogen gas was found to be about 2.0×10^{-5} mol/sec.m².Pa. Permeance to various gases was found to be relatively unchanged from the room temperature values for thermal treatments up to 600°C. However, when the γ -alumina membrane was subjected to temperatures higher than 600°C, the permeance was found to change continuously at constant temperature. This was probably due to a gradual phase transformation of the material, as γ -alumina is known to undergo phase changes at these higher temperatures. Since the temperature required for methane coupling reactions is in excess of 750°C, γ -alumina may not be the ideal candidate since a leveling off of permeance is not realized.

B3.4 Zirconia Membranes

Zirconia membranes are stable at high temperatures, and are also available in pore sizes of less than 2000 Angstroms, but zirconia itself is a low level methane conversion catalyst allowing methane conversion to CO_x products. Studies in the literature have shown that though the zirconium-containing complex oxides catalyze the methane oxidative coupling reaction, they are not very active catalysts. Of all the zirconium containing catalysts, zirconia itself is the least effective. Khan and Ruckenstein [1] reported methane conversion of 2.4% , with a C_2 yield of 0.43% and C_2 and CO_x selectivity of 18% and 82% respectively at 750°C and CH_4/O ratio of 4.

Perovskite depositions on 1000 Angstrom zirconia membranes gave results similar to the ones in the α -alumina experiments. Complete pore closure was not achieved, though a drop in permeance of gases through the membrane was observed. A comparison with different pore size zirconia membranes, and the 2000 Angstrom alpha alumina membrane is made in Figure 9, showing the permeance of nitrogen gas through these different membranes that have been subjected to three perovskite (0.6M) depositions and treated at 200°C. Even though alpha alumina has a bigger pore size (2000 Angstrom), at the completion of the three depositions and thermal treatment, the permeance value is lower in this alpha alumina membrane than the smallest pore size (200 Angstrom) zirconia membrane, possibly indicating better wettability of alumina than zirconia.

B4. Dense Membrane Preparation and Characterization

B4.1 Preparation Procedure

- Synthesis of $\text{La}_{0.2}\text{Sr}_{0.8}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (perovskite) using ethylene-glycol technique.
- Cold-Uniaxial compression of synthesized perovskite at 1500 MPa. pressure
- Calcination of pellet at 1200 C.
- Pellet welded to 10mm O.D. quartz tube using gold foil seal.

B4.2 Characterization Results :

- Oxygen permeation measurements with varying temperature.
- Steady state oxygen permeation measurements at constant temperature.

APPENDIX C : POROUS VYCOR MEMBRANES: PROPERTIES AND CHARACTERIZATION

C1. Physical and Chemical Properties of porous Vycor®

Chemically, porous VYCOR is 96% silica and the remainder is chiefly boric oxide. It has an average pore diameter of 50 Angstroms with a voidage of about 28% of its total volume. Porous VYCOR can adsorb water vapor up to 25% of its dry weight and gives up this water when heated or placed in a dry atmosphere.

The starting material for the fabricated membranes was commercially available porous Vycor tubes. Tubes of dimensions of 10 mm OD, 7mm ID and 100 cm long were purchased from Corning Inc. (Code 7930). The membranes had an average pore diameter of 40Å with a void fraction of about 28%.

C2. Gas Permeance Measurements through porous Vycor membrane tubes.

Figure C-2 shows the steady state permeability of nitrogen gas at room temperature through Vycor tubes which were pre-treated at various temperatures. The pre-treatment procedure involved calcination of the Vycor tubes at a fixed temperature for 48 hours. Gas permeability through the membrane decreased rapidly with increasing pre-treatment temperature between 850°C and 1000°C. Though there was a significant change in gas permeability through the membrane in this temperature range, at a fixed temperature, this permeability was constant at steady state. Thus, gas permeability through the porous Vycor membrane tubes could be adjusted by controlled calcination of the membrane material. At temperatures below the pre-treatment temperature, gas permeability through the membrane were found to remain steady at a constant operating temperature, over extended lengths of time. Since a typical experimental run would last

between 24 and 48 hours and would be carried out at temperatures lower than 850°C . all the Vycor membranes were pre-treated at 900°C for 48 hours before use in each experiment.

Figure C-2. Permeability measurements on porous Vycor membrane with nitrogen gas.

C3. Shrinkage Measurements on Vycor Tubes

The cause for the lowered gas permeability through the porous Vycor tubes at higher pre-treatment materials was due to collapse of the pores in the material. This pore collapse excludes the voidage in the material and the material shrinks. It was important to accurately measure the amount of radial and linear shrinkage that the porous Vycor tubes undergo since this information is critical in developing a fabrication procedure for membranes reactors using porous Vycor tubes as the inorganic membranes in the reactors.

Along with these gas permeability measurements, linear shrinkage measurements were also performed on the porous Vycor membrane tubes. Figure 3 shows that the linear shrinkage is about 2.5% at 850°C and about 6.35% at 1000°C. This data corresponds to the temperature range where a steep drop in steady state gas permeability through the membrane was observed (Appendix C2). A knowledge of the shrinkage characteristics and of the systematic variation of the gas permeability through the porous Vycor material, was utilized in devising the porous membrane module fabrication procedure discussed in Appendix C6.

Figure C-3. Linear shrinkage measurements on porous Vycor membrane with increasing temperature.

C4. Pore Size Measurements in porous Vycor

Nitrogen physisorption was used to measure pore volumes, adsorption/desorption isotherms and BET surface areas of the porous Vycor material on an Autosorb-1c instrument (Quantachrome Co.). Pore size distributions were calculated from a desorption branch of the adsorption/desorption isotherm according to the BET theory.

Samples were prepared by drying the membrane tube to 80°C , grinding and sieving to 60-80 mesh size. Figure 4 shows the pore size distribution in porous Vycor membranes before and after thermal pre-treatments at 850°C . A very sharp distribution, with the peak position at $40\text{\AA}$ was observed for fresh Vycor. This pore size distribution remained unchanged even after the porous Vycor was pre-treated at 850°C . The drop in pore volume from 0.25 cc/gm to 0.025 cc/gm , indicated that only total collapse of pores occurred with increasing temperature.

Figure C-1. Pore size distribution in porous Vycor before and after thermal treatment at 900°C.

C5. POROUS VYCOR MEMBRANE PREPARATION

Porous VYCOR was the chosen membrane for use in the membrane reactors to study the oxidative coupling of methane due to the fact that controlled calcination of these membranes permits the gas permeance to be adjusted to values appropriate for methane coupling. The ability to obtain reasonable gas permeation, with a pressure differential maintained across the membrane, facilitates metering of oxygen flow for our studies on oxidative coupling of methane in membrane reactors.

A composite five sectional Vycor-Quartz membrane module served as the tube of the shell-and-tube reactor. The membrane module consists of a well defined central porous region with a permeability to nitrogen of 20,000 barrer, porosity minimized sections on either side of the central porous region with a permeability of about 200 barrer, and two 10 mm O.D. quartz tube end sections. On the basis of the results on material characterization, the following fabrication procedure was devised. A 30 cm long porous Vycor tube was first pre-treated at 900°C for 24 hours. The porosity minimized sections were then made from this pre-treated tube by subjecting ~ 10 cms from the two ends to an additional thermal treatment at 1100°C for 24 hours. The Vycor tube was then cut so that the porous section is centered. The two end sections were then glass-welded onto two non-porous quartz tubes of 10 mm O.D. and of equal length to make up a five-sectional membrane module with a total length of 52 cms. The lengths of the porous section could be varied just by subjecting different lengths of the Vycor material at the higher temperatures, but a typical membrane module, the porous section was about 10 cm and the porosity reduced sections was about 7 cms. The transition region between the porous central region and the porosity reduced Vycor was generally limited to less than 1 cm. The constant pore size all through the porous section minimized the radial and axial inhomogenities in the amounts of oxygen permeate flow along the porous section.

C5.1 Porous Vycor membrane module Fabrication Procedure

The porous Vycor membrane module is composed of a well defined central porous region, capped on either end by relatively non-porous Vycor membranes. On the basis of the results on material characterization, the following operating procedure is recommended for membrane module fabrication.

- Cut the porous Vycor membrane tube (10 mm. O.D, 7 mm I.D.) to a length of 30 cms.
- Place the entire tube in the 4 foot Lindberg (Tube) Furnace and heat at 900°C for 48 hours. Heat increments should be very gradual, at a step rate of 30°C per 30 min. Cool down can be a little faster, at a step down rate of 100°C in 60 minutes.
- Heat each end of the above tube at 1100°C . This can be achieved by sticking the tube partially into the hot zone and using the thermocouple to monitor the temperature in the hot zone. Follow the same heat and cool cycle as above.
- The three section tubes can then be sent to a glass blower, with instructions to cut either end of the three section tube such that the porous Vycor is centered. Two quartz tubes of 10 mm O.D. should then be attached at either end of the three sectional membrane so that the total length of the membrane module comes exactly to 52cm(± 0.25 cms).

Appendix D

Theoretical Calculation for finding the “Diffusional Regimes” of operation in the Radial Flow Reactor Experiments.

D1. Effect of Flow Regime on Reactivity

1. With reference to the literature that reported the high tendency of desired products further oxidizing with catalyst site contact, discuss the theoretical benefits of a larger pore system in the viscous flow regime over a smaller pore membrane which would place the reacting gases in the Knudsen flow regime.
2. Discuss calculation of Knudsen vs. viscous flow for porous tubes.
3. Show table of calculation results that shows the 5.0 μm to be approximately 53 % in viscous flow and the 0.02 μm tube to be less than 1 % viscous flow.
4. Hypothesize about potential selectivity benefits of larger pore system due the minimization of product contact with active sites and the detrimental effects of the smaller pore systems due to more intimate contact of products with the active sites.

Table 2. Flow regimes [λ = molecular mean free path, r = pore radius]

$T = 800^\circ\text{C}$

$P = 1 \text{ atm}$

Pore Diameter (μm)	Kn λ/r	Flow Regime
2.0	0.2	Viscous
0.2	2.0	Transition
0.02	20	Knudsen

Appendix E

Radial Flow Catalytic Membrane Reactor

E.1 Catalytic Membrane Reactor Fabrication

The catalytic membrane reactor was fabricated by joining together a porous alpha alumina ceramic tube membrane with a non-porous alpha alumina tube. Feed gases entered from the opening on the non-porous tube and reacted with the catalyst deposited in the pores of the alpha alumina porous membrane. The resulting flow pattern, flowing radially outward from the membranetube gave the name “catalytic radial flow membrane reactor” to this reactor design. Figure E-1 shows a side view of the catalytic membrane module.

The complete reactor assembly was constructed by joining a nonporous long cylindrical piece of non-porous Al_2O_3 tubing to a shorter membrane piece of porous alumina. The porous material consisted of α -alumina supports of 12-15 μm pore diameters with membrane toplayers of 0.02, 0.05, 0.2, 0.5, 2.0, and 5.0 μm pore diameters. The toplayers were located on the inner diameter of the porous tubes. The porous material had dimensions of 7.00 mm inner diameter, 10.00 mm outer diameter. The membrane and the nonporous materials were cut to length using a glass cutting wheel.

Figure E-2. Cross-section of the porous reactor tube support, including glaze bond, the combination glaze and adhesive plug.

The manufacture of the entire reactor tube structure was intended to create a reactor assembly large enough to place the active catalyst within the heated reaction zone of the heater. The section of porous alumina was bonded to the longer, non-porous section of tubing using a nonporous proprietary ceramic glaze. The end of the porous tube not joined to the non-porous handle was sealed off using a porous ceramic adhesive and the ceramic glaze used earlier. This created a unit of overall length 17.5 cm, with a 2.6 cm porous tip and one major opening, at the non-porous end (see Figure E-1). An additional reactor of 5.0 μm pore diameter was constructed with a shorter length of 0.7 cm for the porous section.

Figure E-1. The welded porous tube reactor assembly: (1) is the 14.5 cm non-porous section, used as an extension handle for the active section; (2) is a bond made of a ceramic glaze; (3) is the 2.6 cm porous section used as the catalyst support; and (4) is a combination adhesive/glaze cap.

Figure E-3. Cross-section of the porous tube after sealing the ends with glaze.

The porous and non-porous lengths of tubing were cut using a glass cutter. One end of the non-porous tubing was beveled so that when the two tubes were connected a groove resulted which allowed more surface area of the nonporous

Figure E-2).

The axial ends of the porous tube were coated with the glaze (see Figure E-3). After the coating glaze was cured, additional coatings were applied until a consistent, crack-free surface was produced. The porous and non-porous tubes were placed next to each other in a holder, their ends just touching, and the glaze was spread into the groove. This was allowed to cure and then patched with additional coats until there were no visible cracks or imperfections in the glaze. The ceramic adhesive was applied to the open end of the porous tube using a paint brush, drawing a film across the opening. This was hardened in a vertical position, with the closed end down, for an hour, heated to 65°C for four hours, and finally cured at 200°C for two hours. When it was cooled, the glaze was applied over the porous adhesive which sealed any pores and holes.

The glaze was a proprietary mixture containing various metal-oxides. It was applied wet, allowed to dry at ambient temperature, and then set in an oven. The temperature of the oven was ramped up to 1200°C at a rate of 8°C/min., held at 1200°C for 20 minutes, and then allowed to cool to room temperature at the same rate (8°C/min.).

The glaze melted during this curing process and filled any large openings or cracks while setting to a glassy white, hard substance.

It was found that the glaze provided a relatively strong bond between the porous and non-porous tubings and resisted cracking during large temperature changes, so the adhesive was not needed to bond the tubes together. However, the wet glaze was not cohesive enough to form a film across an opening as large as that at the end of the tubing, so the adhesive was needed as a back support for the glaze in this procedure.

E.2 Packed Bed Reactor Fabrication

Three conventional packed bed reactors (PBRs) were studied. The PBRs were constructed by sliding one nonporous Al_2O_3 tube within a slightly larger diameter nonporous Al_2O_3 tube and then welding the two tubes together at the opening in the middle with the ceramic nonporous glaze. The purpose of using two tubes was to utilize the larger volume of the larger tube within the heated zone of the furnace as the location of the packed bed. The bottom opening of the tube end (where the packed bed was placed) was sealed with a 5.0 μm pore diameter $\alpha\text{-Al}_2\text{O}_3$ porous disk. This 5.0 μm $\alpha\text{-Al}_2\text{O}_3$ porous disk was welded to the bottom of the nonporous tube with the ceramic glaze as shown in the schematic. Characteristics about the different PBRs can be found in Table E.1 and Table E.2. Table E.3 lists the size equivalent in millimeters for the Tyler Equivalent Mesh Size of the packing material.

Table E.1. Characteristics and dimensions of packed bed reactor.

PBR #	Catalyst Amount (g)	Quartz Chips (g)	Bed Height (cm)	Bed Diameter (cm)	Bed Volume (cm ³)
1	0.2	2	2.0	0.96	1.45
2	0.2	2	2.0	0.96	0.724
3	0.1	1	1.0	0.96	0.724

Table E.2. Size of catalyst and quartz chip packing for the packed bed reactors.

	<i>Tyler Equivalent Mesh Size</i>	
PBR #	Catalyst	Quartz Chips
1	60/80	16/30
2	60/80	60/80
3	60/80	60/80

Table E.3. The size equivalent for the Tyler Equivalent Mesh Size.

Tyler Equivalent Mesh Size	Size (mm)
60/80	0.25/0.18
16/30	1.19/0.59

Schematic of a cross sectional view of the non-porous packed bed reactor.

Two additional packed bed reactors were studied using the porous section of one of the porous tube reactors for the packing material. The porous section of the tube reactor, already deposited with catalyst, was crushed up into small fragments and used as the packing for these packed bed investigations. The first packed bed reactor, PBR #4, consisted of only the 60/80 mesh size material of the crushed porous tube reactor. It was desired to use the same mesh size packing, 60/80, as the previous two packed bed reactions, PBR #1 and #2. However, it was possible to recover only a small amount of this 60/80 mesh size material. This resulted in a relatively small PBR #4 in comparison to the previous packed bed reactors (see Table E.4). In an effort to perform this reaction with more material, hence more catalyst and higher conversions, another packed bed reactor, PBR #5, was investigated using additional smaller mesh size fractions of the crushed porous tube. The specifications for these packed bed reactors can be found in Table E.4, Table E.5, and Table E.6.

Table E.4. Characteristics and dimensions of packed bed reactors #4 and #5.

PBR #	Amount of Crushed Material (g)	Catalyst Amount (g)	Bed Height (cm)	Bed Diameter (cm)	Bed Volume (cm ³)
4	0.2833	0.0085	0.1	0.96	0.0724
5	0.9113	0.0273	0.7	0.96	0.517

Table E.5. Size of catalyst and quartz chip packing used for the packed bed reactors #4 & #5.

PBR #	Mesh Size of Material	% Mass of Total Packing Material
4	60/80	100
5	60/80	31.1
5	80/120	21.5
5	120/140	13.1
5	140/230	34.3

Table E.6. Catalyst characteristics of the packed bed reactors.

PBR #	<i>Catalyst</i>	
	Source	Form
4	(Sm(NO ₃) ₃ •6H ₂ O	Cubic
5	(Sm(NO ₃) ₃ •6H ₂ O	Cubic

E.3 SEM Cross-Sectional Views of Porous Reactor Tubes

The membranes used as catalyst supports for the porous tube reactors were observed using SEM (see Figure E.4-Figure E.9). The membrane toplayers for each pore size were located on the inside diameter of the cylindrical porous tubes. The supports for all membranes were made of $\alpha\text{-Al}_2\text{O}_3$ with a cross-sectional thickness of 1.5 mm. The 5.0 μm pore diameter tube has a toplayer of material observed to only slightly smaller than the support. All other pore size tubes had a distinctive single toplayer with an approximate thickness of 20-30 μm except for the 0.02 μm pore diameter asymmetric membrane tube which had an additional intermediate layer.

Figure E.4. SEM cross-section of the 5.0 μm pore diameter porous tube.

Figure E.5. SEM cross-section of the 2.0 μm pore diameter porous tube.

Figure E.6. SEM cross-section of the 0.5 μm pore diameter porous tube.

Figure E.7. SEM cross-section of the 0.2 μm pore diameter porous tube.

Figure E.8. SEM cross-section of the 0.05 μm pore diameter porous tube.

Figure E.9. SEM cross-section of the 0.02 μm pore diameter porous tube.

E.3.1 5.0, 0.5, 0.05 μm Pore Diameter Reactors

In an effort to investigate the potential benefits of increasing the linear velocity on methane conversion rates and C_2 selectivity, both a 5.0 μm short tube reactor (0.7 cm) and a 5.0 μm long tube reactor (2.6 cm) were investigated. Due to the smaller cross-sectional surface area available for flow in the shorter reactor for a given feed flowrate, the shorter 5.0 μm reactor resulted in higher linear velocities than the 5.0 μm long tube reactor. The linear velocity of the porous tubes was defined as the volumetric flowrate of the feed divided by the cross-sectional area within the inside diameter of the porous tube reactor which could allow the passage of gas flow.

In addition, smaller pore size reactors were also studied to investigate the relationship of pore size on reactivity. The pore sizes used were a 0.5 μm pore diameter (2.6 cm length) and a 0.05 μm (2.6 cm length) pore diameter reactor. Characteristics about all four of these reactors can be found in Table E.7.

Table E.7. Reactor characteristics for the 5.0 μm long, 5.0 μm short, 0.5 μm , and 0.05 μm pore diameter reactors.

Pore Diameter (μm)	Reactor Length (cm)	Catalyst Amount (mg)	Toplayer Composition
5.0	2.6	103.9	$\alpha\text{-Al}_2\text{O}_3$
5.0	0.7	30.3	$\alpha\text{-Al}_2\text{O}_3$
0.5	2.6	93.9	$\alpha\text{-Al}_2\text{O}_3$
0.05	2.6	55.6	ZrO_2 and $\alpha\text{-Al}_2\text{O}_3$

APPENDIX F

EXPERIMENTAL RESULTS WITH RADIAL FLOW CATALYTIC MEMBRANE REACTORS

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F1. Catalyst (Sm_2O_3) Characterization

X-Ray Diffraction was used to identify the form (phase) of the Sm_2O_3 used for the experimental studies both in the conventional packed bed reactors, as well as the catalytic membrane reactors. The diffraction patterns obtained by XRD for the catalyst used for methane coupling studies in each packed bed, before and after reaction, were compared with JCPDS listings for Sm_2O_3 in order to determine whether the catalyst was in the monoclinic or the more active cubic phase. The monoclinic form of the Sm_2O_3 catalyst was obtained by calcining the purchased Sm_2O_3 powder catalyst (purchased from Aldrich Chemical Co. , Cat. # 22,867-2) . The cubic form of the Sm_2O_3 catalyst was obtained from calcination of the samarium nitrate (aqueous solution of samarium nitrate was used for synthesizing the catalyst).

The catalytic activity of the two forms of Sm_2O_3 was studied by packing the catalyst mixed with quartz chips in a non-porous tube and carrying out the high temperature methane coupling reaction. Non-porous packed bed reactor #1 contained the monoclinic form while the non-porous packed bed reactors #2 and #3 contained the cubic form of Sm_2O_3 . Figure 1.1 shows evidence that the catalyst used in PBR #1 was monoclinic before and after the reaction. The monoclinic form of the Sm_2O_3 catalyst showed lower methane conversions at very low hydrocarbon selectivities (see Section 4.3). The cubic form of Sm_2O_3 was obtained by calcining dissolved samarium nitrate to 850°C (see Figure 1.2). As shown in Figure 1.3 and Figure 1.4, the cubic form of the catalyst was maintained throughout packed bed reactions #2 and #3. PBRs #2 and #3 exhibited higher methane coupling activity at higher hydrocarbon selectivity (see section 4.4).

Figure 1.1. XRD of the catalyst used in PBR #1 showing the monoclinic form.

Figure 1.2. XRD of the catalyst used in PBR #2 and #3 showing the cubic form.

Figure 1.3. XRD of the catalyst used in PBR #2 before and after reaction.

Figure 1.4. XRD of the catalyst used in PBR #3 before and after reaction.

F2. 5.0 μ and 0.5 μ pore size reactors

F2.1 Results from permeation study on alumina porous membranes

Ambient temperature permeation of helium through the porous tube reactors was recorded before and after catalyst deposition. A decrease in permeance due to pore filling by the catalyst was observed when the porous tubes were deposited with Sm_2O_3 . Figure 2.5-Figure 2.8 show the permeation results for the 2.6 cm long 5.0 and 0.05 μm pore diameter reactors and the shorter 0.7 cm long 5.0 μm pore diameter reactor before and after catalyst deposition. The relatively horizontal permeation line observed in Figure 2.8 for the 0.05 μm pore diameter reactor after catalyst deposition is indicative of the gas flow being in the Knudsen regime. On the other hand, the sloped or irregular permeation patterns observed in Figure 2.5-Figure 2.7 suggest the flow to be more viscous than Knudsen.

Figure 2.5. Helium permeation through the 5.0 μm blank porous tube reactor at ambient temperature.

Figure 2.6. Helium permeation through the 5.0 μm catalyst deposited porous tube reactor at ambient temperature.

Figure 2.7. Helium permeation through the $5.0\text{ }\mu\text{m}$ (length = 0.7 cm) blank and $0.05\text{ }\mu\text{m}$ blank porous tube reactor at ambient temperature.

Figure 2.8. Helium permeation through the 5.0 μm (length = 0.7 cm) and 0.05 μm porous tube reactors with catalyst at ambient temperature.

F2.2 Blank (Without Catalyst) Reaction Results

Before the methane coupling experiments were performed with the active catalyst, blank reactor runs with the undeposited porous tube reactor were studied to determine the relative reactivity of the reactor set-up without catalyst. The methane conversions observed for the blank porous tubes of all pore sizes, 5.0 long, 5.0 short, 0.5, and 0.05 μm , were small. At the lowest flowrates (highest residence times) the methane conversion was less than 3 % for all pore sizes (see Figure 2.9).

Figure 2.9. Blank reactor methane conversions for the 5.0 μm (long), 5.0 μm (short), 0.5 μm , and 0.05 μm pore diameter reactors.

F2.3 Reaction Results with Catalyst

F2.3.1 Stability Behavior

The stability of the Sm_2O_3 catalyst was investigated by reacting a catalyst deposited reactor tube over a period time and recording changes in reactivity. It was observed that when a $0.5\ \mu\text{m}$ pore diameter reactor (2.6 cm, 92.8 mg catalyst) was reacted over a period of six days that the catalyst did not deactivate. In addition, the methane conversion and total C_2 selectivity was relatively stable with time on-stream.

Figure 2.10. Stability check showing methane conversion, total C_2 selectivity, and C_2 yield vs. elapsed reaction time for the $0.5\ \mu\text{m}$ pore diameter reactor.

F2.3.2 Reactivity Comparison

After catalyst was deposited within the porous tube reactors, the reaction was carried out at a maximum temperature of 800°C and the product composition was

determined using gas chromatography. The reaction was performed at five different flowrates which allowed a range of space velocities to be studied. The reaction results for these four porous tube reactors are included in Figure 2.11-Figure 2.15.

Figure 2.11. Total C₂ selectivity vs. WHSV for the 5.0 μm (long), 5.0 μm (short), 0.5 μm, and 0.05 μm pore diameter reactors.

As shown in Figure 2.11, the higher WHSV for the shorter 5.0 μm tube and the 0.05 μm tube was due to the lower catalyst loading of these reactors. The short and long 5.0 μm reactors gave similar C_2 selectivities at similar WHSVs. Overall, the total C_2 selectivities were similar for all pore sizes. In addition, the methane conversion behavior for these reactor sizes were similar, except for the lower conversion results of the 0.5 μm reactor (see Figure 2.12). Also, similar trends to the plot of methane conversion vs. WHSV were observed for the oxygen conversion results (see Figure 2.13). As shown in an overall reactivity plot of total C_2 selectivity versus methane conversion, Figure 2.14, generally similar reactivity behavior was observed for the different pore size reactors. However, slightly higher conversions were observed with the higher loaded 5.0 μm long reactor.

Figure 2.12. Methane conversion vs. WHSV for the 5.0 μm (long), 5.0 μm (short), 0.5 μm , and 0.05 μm pore diameter reactors.

Figure 2.13. O_2 conversion vs. WHSV for the 5.0 μm (long), 5.0 μm (short), 0.5 μm , and 0.05 μm pore diameter reactors.

Figure 2.14. Total C₂ selectivity vs. methane conversion for the 5.0 μm (long), 5.0 μm (short), 0.5 μm, and 0.05 μm pore diameter reactors.

As shown in Figure 2.15, similar methane conversion rates were observed for the different pore size reactors. However, the 0.5 μm pore diameter reactor gave slightly lower methane conversion rates when compared to the other reactors. There was no apparent trend observed between the magnitude of the methane conversion rate at a particular WHSV and the reactor pore size.

Figure 2.15. Methane conversion rate vs. WHSV for the 5.0 μm (long), 5.0 μm (short), 0.5 μm , and 0.05 μm pore diameter reactors.

At the same WHSVs and linear velocities, both the long and short tube reactors had similar methane conversion rates (see Figure 2.16). For a given feed flowrate, the shorter tube with its smaller cross-sectional area for the feed flow to pass through resulted in higher linear velocities. If limitations to mass transfer were in fact limiting the methane conversion rate and these higher linear velocities were able to overcome these limitations, then an increase in the slope of the methane conversion rate might be expected due to the higher linear velocities of the shorter tube. However, the methane conversion rate for the shorter tube did not change from the similar slope of the longer tube (see WHSV of 0-300 hr^{-1} in Figure 2.16) even at the highest linear velocities. Therefore, these results indicate that with these porous tube reactors, the benefits of increasing the linear velocity to increase methane conversion rates were not observed.

Figure 2.16. Methane conversion rate comparison with linear velocities for the 5.0 μm long and short reactors.

F3. OCM studies with 2.0, 0.2, 0.02 μm Pore Diameter Reactors

In addition to the 5.0, 0.5, and 0.05 μm pore diameter reactors, five more reactors, a 2.0 μm , 0.2 μm , and three different 0.02 μm pore diameter reactors were studied to investigate the relationship of pore size with overall reactivity characteristics. The characteristics of these reactors are shown in Table 3.1.

Table 3.1. Reactor characteristics for 2.0 μm , 0.2 μm , and the three different 0.02 μm pore diameter reactors.

Reactor #	Pore Diameter (μm)	Reactor Length (cm)	Catalyst Amount (mg)	Toplayer Composition
-----	2.0	2.6	99.6	$\alpha\text{-Al}_2\text{O}_3$
-----	0.2	2.6	98.5	$\alpha\text{-Al}_2\text{O}_3$
1	0.02	2.6	97.3	ZrO_2 and $\alpha\text{-Al}_2\text{O}_3$
2	0.02	2.6	103.8	ZrO_2 and $\alpha\text{-Al}_2\text{O}_3$
3	0.02	2.6	94.6	ZrO_2 and $\alpha\text{-Al}_2\text{O}_3$

F3.1 Permeation Studies

Ambient temperature permeation through the different pore size reactor tubes was observed before and after catalyst deposition. A decrease in permeance due to pore filling by the catalyst was observed when the porous tubes were deposited with Sm_2O_3 . The 2.0 μm pore diameter reactor gave permeation results that were not indicative of the gas flow being in the Knudsen regime (see Figure 3.17 and Figure 3.18). However, in contrast, Figure 3.19 and Figure 3.20 show the clear transition of the 0.02 μm pore diameter reactors to the Knudsen flow regime from viscous flow when catalyst was present in the reactors. This was indicated by relatively horizontal permeation results observed in Figure 3.20.

Figure 3.17. Helium permeation through the 2.0 μm blank porous tube reactor at ambient temperature.

Figure 3.18. Helium permeation through the 2.0 μm porous tube reactor with catalyst at ambient temperature.

Figure 3.19. Helium permeation through the 0.02 μm Reactor #2 and #3 blank porous tube reactors at ambient temperature.

Figure 3.20. Helium permeation through the 2.0 μm and 0.02 μm #1, #2 and #3 porous tube reactors with catalyst at ambient temperature.

F3.2 Blank (Without Catalyst) Reaction Results

Before the methane coupling experiments were performed with the active catalyst, blank reactor runs with the undeposited porous tube reactors were studied to determine the relative reactivity of the reactor set-up. The methane conversions were low for the blank porous tubes of all pore sizes, 2.0, 0.2, and the three 0.02 μm pore diameter reactors. At the lowest flowrates (highest residence times), the methane conversion was less than 4 % for all pore sizes (see Figure 3.21)

Figure 3.21. Blank reactor methane conversions for the 2.0 μm , 0.2 μm , and 0.02 μm pore diameter reactors.

F3.3 Reaction Results with Catalyst

F3.3.1 Stability Behavior

It was observed for the 0.02 μm pore diameter reactors that the reactivity changed with time on-stream. These results contrasted to the earlier presented stability results for the 0.5 μm pore diameter reactor. The 0.5 pore diameter reactor total C_2 selectivity and CH_4 conversion remained stable over a six day period. The 0.02 μm pore diameter reactors, Reactor #2 and Reactor #3, showed increasing total C_2 selectivities with time on-stream and only minor catalyst deactivation with the methane conversions remaining stable (see Figure 3.22). However, the total C_2 selectivity for the 0.02 μm pore diameter reactors did not increase indefinitely with continued time on-stream. The reactivity of these two reactors, Reactor #2 and #3, with continued reaction time reached a final steady-state in which the total C_2 selectivity stopped increasing.

In contrast to the observed trend of the 0.02 μm pore diameter reactors, the total C_2 selectivity for the 2.0 μm reactor remained relatively unchanged with time on-stream (see Figure 3.23). It should be noted that the stability behavior of the 0.02 μm , Reactor #1 which gave the lowest total C_2 selectivity of the three 0.02 μm pore diameter reactors was not able to be investigated with further time on-stream due to a pinhole leak in the weld.

As presented earlier, the toplayer composition of the smaller 0.02 μm pore size reactors was fabricated out of a mixture of ZrO_2 and $\alpha\text{-Al}_2\text{O}_3$, whereas the membranes of the larger pore size reactors were composed of pure $\alpha\text{-Al}_2\text{O}_3$. The trends of higher C_2 selectivities with time on-stream were observed for the reactors having a mixture of ZrO_2 and $\alpha\text{-Al}_2\text{O}_3$ rather than the pure $\alpha\text{-Al}_2\text{O}_3$. In regards to the toplayer composition of the 0.02 μm tubes, the reactivity and stability differences might have resulted from different catalyst interactions with the zirconia mixture toplayer. The membrane micro-structure might have been affected in the catalyst deposited 0.02 μm pore diameter reactors. Also, the dispersion of catalyst within the porous tubes might have affected the reactivity results. These differences in the 0.02 μm pore diameter reactors might explain the observed trends for the different reactors.

Numerous experiments were performed to investigate whether reaction set-up experimental methods were causing the changes in the reactivity results for the 0.02 μm reactors. For instance, the reactors were heated up under either atmospheric air or flowing helium for different periods of time before reacting. Also, after particular reaction runs, the reactors were cooled down, disassembled, and then reassembled for sequential reaction runs. The result was that changes in reaction set-up did not appear to affect the final steady-state reactivity values of the 0.02 μm reactors.

Figure 3.22. Stability behavior of the three 0.02 μm pore diameter reactors.

Figure 3.23. Stability behavior of the 2.0 μm pore diameter reactor.

F3.3.2 Reactivity Comparison

Reactivity results will compare the final steady-state values for the 0.02 μm pore diameter reactors, Reactor #2 and #3, the only results obtained for the 0.02 μm pore diameter Reactor #1, and the initial run values for the 2.0 and 0.2 μm pore diameter reactors. As shown in Figure 3.24. Total C₂ selectivity vs. WHSV for the 2.0 μm , 0.2 μm , and the three 0.02 μm pore diameter reactors.

and Figure 3.27, the three different 0.02 μm pore diameter reactors showed markedly different total C₂ selectivities, whereas the 0.02 μm Reactor #3, and the 2.0 and 0.2 μm reactors showed similar C₂ selectivities. The reactor which gave the highest total C₂ selectivities, 0.02 μm Reactor #2, also had the lowest methane and oxygen conversion at a given WHSV when compared to the other reactors (see Figure 3.25 and Figure 3.26, respectively). The 0.2 μm reactor tube had the highest methane and oxygen conversions while the 0.02 μm Reactors #1 and #3, along with the 2.0 μm , showed similar methane and oxygen conversions. The differences in reactivity between the 0.02 μm reactors might have resulted from differences in the catalyst dispersion within the porous structures of the three different reactors or differences in the interaction of the catalyst with the toplayer.

As presented in Figure 3.28, the 0.02 μm reactors showed similar methane conversion rates, while the largest difference was that of the 0.2 μm pore diameter reactor which gave the highest methane conversion rates when compared to the lowest 2.0 μm pore diameter reactor. The methane conversion rates for these three different pore size reactors did not follow any trend with regards to the pore size of the reactors.

Figure 3.24. Total C₂ selectivity vs. WHSV for the 2.0 μm, 0.2 μm, and the three 0.02 μm pore diameter reactors.

Figure 3.25. Methane conversion vs. WHSV for the 2.0 μm, 0.2 μm, and the three 0.02 μm pore diameter reactors.

Figure 3.26. Oxygen conversion vs. WHSV for the 2.0 μm, 0.2 μm, and the three 0.02

μm pore diameter reactors.

Figure 3.27. Total C₂ selectivity vs. methane conversion for the 2.0 μm, 0.2 μm, and the three 0.02 μm pore diameter reactors.

Figure 3.28. Methane conversion rate vs. WHSV for the 2.0 μm , 0.2 μm , and the three 0.02 μm pore diameter reactors.

F4. Packed Bed Reactors (Quartz Chips & Powder Catalyst)

The purpose of the packed bed reactions was to compare the overall reactivity of the porous tube reactors to reaction results obtained using conventional packed bed configurations. It was desired to observe and compare the C_2 selectivity, methane conversion, and methane conversion rates at particular WHSVs. A comparison of methane conversion rates at particular WHSVs provided insight on the relative effectiveness of the two different reactor configurations.

However, it should be noted that in using two different reactor configurations for a comparison that many reaction parameters are not held constant. Parameters such as the residence time of the gases within the different reactors due to different reactor lengths and changes within the internal apparatus make direct comparisons between these reactor configurations difficult and challenging. The characteristics of the three different conventional packed bed reactors (PBRs) investigated are found in Table 4.2-Table 4.4.

**Table 4.2. Characteristics and dimensions of packed bed reactors #1, #2, and #3
(conventional PBRs)**

PBR #	Catalyst Amount (g)	Quartz Chips (g)	Bed Height (cm)	Bed Diameter (cm)	Bed Volume (cm ³)
1	0.2	2	2.0	0.96	1.45
2	0.2	2	2.0	0.96	0.724
3	0.1	1	1.0	0.96	0.724

Table 4.3. Size of catalyst and quartz chip packing for the packed bed reactors #1, #2, and #3 (conventional PBRs)

PBR #	<i>Tyler Equivalent Mesh Size</i>	
	Catalyst	Quartz Chips
1	60/80	16/30
2	60/80	60/80
3	60/80	60/80

**Table 4.4. Catalyst characteristics of the packed bed reactors #1, #2, and #3
(conventional PBRs)**

PBR #	<i>Catalyst</i>		
	Amount (g)	Source	Form
1	0.2	Sm ₂ O ₃ powder	Monoclinic
2	0.2	(Sm(NO ₃) ₃ •6H ₂ O	Cubic
3	0.1	(Sm(NO ₃) ₃ •6H ₂ O	Cubic

F4.1 Blank (Without Catalyst) Reaction Results

An experiment was performed to assess the amount of reactivity in the packed bed reactor apparatus without catalyst present. Figure 4.29 shows that the blank reactor conversion at the lowest flowrate was less than 4 %. The packed bed blank reactor methane conversions were similar to the blank reactor results obtained for the porous tube reactors.

Figure 4.29. Blank reactor (no catalyst) methane conversions for the packed bed reactor.

F5. Packed Bed Reactor (Using Crushed Porous Tube Reactor Material)

F5.1 Reaction Temperatures

Similar to the temperature recording of the porous tube reactors, the observed temperature of the packed bed reactions was the maximum reaction temperature, rather than the heater temperature. Typical temperature profiles for the packed bed reactors are shown in Figure 5.30.

Figure 5.30. Temperature profiles observed in packed bed reactors.

F5.2 Comparison Studies

The purpose of the packed bed reaction using the crushed porous material of the reactor tube from the previously run highest selectivity 0.02 μm Reactor #2 was to compare the effectiveness of two different reactor configurations, a packed bed reactor and a radial flow porous tube. The goal was to minimize the differences between the packed bed reactor and the porous tube to make a more direct comparison between the two reactor configurations. If higher methane conversion rates were observed for the radial flow configuration, it might be concluded that the porous tube configuration provides a more effective support material for the catalyst.

Due to the limited amount of a particular sieved mesh size of the 0.02 μm Reactor #2 porous tube after it was crushed, two packed bed reactions were performed. It was initially desired to maintain the same size packing of 60/80 mesh size that was used in the previously run conventional packed bed reactors, #2 and #3. Packed Bed Reactor #4 consisted of all the crushed material able to be collected in the 60/80 mesh size. The amount of this material was a small 0.2833 g which gave a catalyst amount of 8.5 mg. In addition, due to the small amount of material, the bed height was one millimeter.

As a result of the low methane conversions for PBR #4 (see Figure 5.31), an additional packed bed reaction was investigated, PBR #5, which consisted of crushed material of varying mesh sizes. The goal of PBR #5 was to increase the catalyst loading of this crushed porous tube packed bed reactor to catalyst amounts that more closely approached those used in the actual porous tube reactors. Using various mesh sizes increased the catalyst mass to 27.3 mg. The characteristics of PBR #4 and #5 are included in Table 5.5 and Table 5.6.

Table 5.5. Characteristics and dimensions of packed bed reactors #4 and #5 (using crushed porous material).

PBR #	Amount of Crushed Material (g)	Catalyst Amount (g)	Bed Height (cm)	Bed Diameter (cm)	Bed Volume (cm ³)
4	0.2833	0.0085	0.1	0.96	0.0724
5	0.9113	0.0273	0.7	0.96	0.517

Table 5.6. Mass distribution of different packing sizes for the packed bed reactors #4 and #5 (using crushed porous material).

PBR #	Mesh Size of Material	% Mass of Total Packing Material
4	60/80	100
5	60/80	31.1
5	80/120	21.5
5	120/140	13.1
5	140/230	34.3

F5.2.1.1 Reactivity Comparison to Porous Tube Reactor

In all cases, when comparing the 0.02 μm Reactor #2 porous tube to PBR #4 and #5, the results for the porous tube were superior to these packed bed configurations (see Figure 5.31-Figure 5.34). The total C_2 selectivity for the two packed bed reactions, PBR #4 and #5, was substantial lower than the selectivity from the 0.02 μm Reactor #2 porous tube. In addition, the C_2 selectivity for PBR #5, with the various mesh size loadings, was less than PBR #4. As expected, the methane conversion for PBR #5 was higher than PBR #4. Overall, this comparison showed the 0.02 μm Reactor #2 porous tube to have both higher C_2 selectivities and higher methane conversion rates than the packed bed reaction using the crushed tube material from this same reactor.

Figure 5.31. Total C₂ selectivity vs. methane conversion for PBR #4, PBR #5, and the 0.02 μ m porous tube Reactor #2 (which gave the highest C₂ selectivities of the porous tubes).

Figure 5.32. Total C₂ selectivity vs. WHSV for PBR #4, PBR #5, and the 0.02 μm porous tube Reactor #2 (which gave the highest C₂ selectivities of the porous tubes).

Figure 5.33. Methane conversion vs. WHSV for PBR #4, PBR #5, and the 0.02 μm porous tube Reactor #2 (which gave the highest C₂ selectivities of the porous tubes).

Figure 5.34. Methane conversion rates vs. WHSV for PBR #4, PBR #5, and the 0.02 μm porous tube Reactor #2 (which gave the highest C₂ selectivities

APPENDIX G

SEM/EDX Digital Maps of catalytic membrane cross sections.

Figure G.1. EDX digital mapping of Sm, Al, & Zr within the entire cross-section (x65) of the 0.02 μm pore diameter *Reactor #1* which resulted in the *lowest* selectivity results. The image used is located in the lower right frame.

Figure G.2. EDX digital mapping of Sm, Al, & Zr within the entire cross-section of (x65) the 0.02 μm pore diameter *Reactor #2* which resulted in the *highest* selectivity results. The image used is located in the lower right frame.

Figure G.3. EDX digital mapping of Sm, Al, & Zr within the entire cross-section (x65) of the 0.02 μm pore diameter *Reactor #3* which resulted in the *middle* selectivity results. The image used is located in the lower right frame.

Figure G.4. EDX digital mapping of Sm, Al, & Zr within a magnified view (x700) of the toplayer, intermediate layer, and part of the support of tube for the 0.02 μm pore diameter *Reactor #1* which resulted in the *lowest* selectivity results. The image used is located in the lower right frame.

Figure G.5. EDX digital mapping of Sm, Al, & Zr within a magnified view (x700) of the toplayer, intermediate layer, and part of the support of tube for the 0.02 μm pore diameter *Reactor #2* which resulted in the *highest* selectivity results. The image used is located in the lower right frame.

Figure G.6. EDX digital mapping of Sm, Al, & Zr within a magnified view (x700) of the toplayer, intermediate layer, and part of the support of tube for the 0.02 μm pore diameter *Reactor #3* which resulted in the *middle* selectivity results. The image used is located in the lower right frame.aaa

APPENDIX H

Nanoparticulate Synthesis by Cavitation in a Microfluidizer

A novel synthesis technique was employed that uses the cavitational forces that cause the formation of nanometer sized particles of complex stoichiometry to prepare the perovskite materials. This process involved the use of a Microfluidizer which uses the principle of cavitation to synthesize complex oxides.

In a Microfluidizer, a solution of the nitrates of the corresponding oxides constituting the complex oxide is fed into a interaction chamber through a liquid pump at a very slow rate (about 2-5 ml/min). A precipitating agent, usually a hydroxide, (NH_4OH or KOH) that is contained in a reservoir is sucked into the interaction chamber during the suction stroke. A compression stroke of a plunger arrangement then pressurizes the fluid mixture in the interaction chamber to extremely high pressures. Typical operating pressures range from 20,000 psi to 25,000 psi. for complex oxide synthesis. The pressurized product is then split into two streams, channelled through microchannels, and accelerated at very high velocities. The formed jets are then directed toward each other and collide in the "interaction zone". In this small, precisely defined zone, the precipitating hydroxides are subjected to immense forces of impact, cavitation and shear, generated by the micro flow channels and submerged jet impingement. The sudden expansion causes micro-bubble formation, which collapse on pressure release stroke, inducing very high temperatures locally. This localized thermal energy converts the complexed hydroxide into the corresponding oxide. Since the interaction and thermal excitation occurs on a micron scale level, the oxide formation and simultaneous precipitation causes very small particulates of the material. The particle size is in the nanometer range. However, due to the agglomeration of the particulates, grain growth occurs, with the grains typically in the sub-micron size range. The high degree of mixing achieved in the interaction provides excellent compositional uniformity in the product.

The Microfluidizer synthesis not only produces nanometer sized particulates which have very good compositional uniformity, but the complex oxides also have very good phase purity. XRD analysis was used to study the structure of the oxides and perovskites synthesized in the Microfluidizer. Since the particulates that are formed are micro-crystalline, room temperature drying of the product does not exhibit any structural peaks in the XRD. When the product is heated above 200C, any residual hydroxides and nitrates are converted into the oxide. The calcination also causes the grains to grow in size and form crystallites. XRD analysis would then show peaks which can be compared to JCPDS spectra of the corresponding bulk oxides. As the peaks evolve, they are very broad at the lower calcination temperatures. This is because of the X-ray line broadening effect of small particulate systems. The width of the X ray peak (FWHM, full width at half maxima) can be used to calculate the particle size by Debye-Huckel approximation. Another way to ascertain the particle size as well as know the phase purity and crystal structure of the synthesized material is by TEM/SAD (Transmission Electron Microscopy/ Selective Area Microdiffraction) analysis of the product. A combination of both the XRD as well as the TEM/SAD techniques was used to characterize the perovskites synthesized in the Microfluidizer during this research.

The versatility of the Microfluidizer to produce complex oxides of very high structural and compositional purity, as well as the ability to make nanometer size particulates, have both been exploited in our research studies to synthesize materials and explore novel techniques of membrane preparation. A series of oxygen conducting perovskites of the family $\text{Sr}_x\text{La}_{(1-x)}\text{FeO}_3$ ($0 < x < 1$), have been synthesized in the Microfluidizer and characterized by XRD. Another research effort concentrated on taking advantage of the small particulate size by depositing the Microfluidizer synthesized oxide particles in porous supports. Nanoparticles of LaAlO_3 were synthesized in the microfluidizer and deposited inside the 2000 Angstrom pore diameter porous Alpha alumina support.